Accelerated wear protocols for understanding clinical wear in modern hip prostheses

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Statement of Originality

I, Danielle de Villiers, confirm that the research included within this thesis is my own work or that where it has been carried out in collaboration with, or supported by others, that this is duly acknowledged below and my contribution indicated. Previously published material is also acknowledged in Appendix D.

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Abstract

Success of total hip replacements is well reported however, failures as a result of wear processes and the biological response to these products continue to challenge the orthopaedic community. Lately, corrosion of metal surfaces as well as wear particles have seen particular interest with elevated blood cobalt levels widely reported in patients receiving metal-on-metal (MoM) hip replacements. Some instances have also reported this in patients with metal-on-polyethylene (MoP) components and these corrosion products are believed to contribute to hypersensitivity reactions reported. This thesis considers wear and cobalt release in MoP and MoM hip bearings tested under standard and challenging hip simulator conditions and includes an exploration of novel bearing coatings to reduce cobalt release. The incorporation of silver into these coatings may be sufficient to produce an antibacterial response, reducing the risk of mid-term infections, another reported cause of failure.

Polyethylene wear was low under standard and clinically relevant adverse conditions in 28mm and 52 mm diameter MoP bearings (less than 35 mm^3/mc). Cobalt release was measurable in 28 mm diameter MoP bearings (51 ppb/mc) with higher levels produced in large 52 mm diameters (123 ppb/mc), the first time this has been reported, although cobalt release was substantially less than that observed in MoM bearings (6909 ppb/mc). Alumina abrasives introduced in the lubricant substantially damaged MoP bearings, increasing the cobalt release to 70,690 ppb after 1 mc, greater than found after edge loaded MoM bearings (19,240 ppb). The removal of these particles still produced elevated cobalt levels compared to standard conditions and increased polyethylene wear to 435 mm^3/mc.

A chromium nitride (CrN) coating in MoP bearings was resistant to this abrasive damage showing no delamination in the coating, with negligible cobalt released after 7.04 mc (153 ppb) and maintained a polyethylene wear rate below 20 mm^3/mc. Silver CrN coatings on both bearing surfaces of MoM components prevented cobalt release under standard conditions, with silver release after 0.17 mc up to 3,720 ppb in high silver surface coatings, although the wear was relatively high (5.24 mm^3/mc). A silver CrN coating with a low concentration of silver at the surface reduced wear and was resistant to 5 mc of edge loading. It generated 241 ppb of cobalt and maintained comparable steady state wear rates (0.65 mm^3/mc) to the uncoated metal while releasing 18,786 ppb silver which may be sufficient to be an effective anti-microbial agent. These coatings may provide potential clinical benefits in MoP and MoM bearings by reducing both wear and cobalt release in ideal and adverse conditions. There may also be beneficial wear products in the form of silver, although further testing of optimised coatings is required.

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1 Introduction

Hip replacements have been in regular use for over 60 years with various material combinations available (Dowson, 2001). The majority of patients receiving a hip replacement can expect a pain free mobility which can last decades (Powers-Freeling, 2013). Patients receiving metal-on-metal bearings, however, have reported increased metal ion levels in the blood and urine as well as in the hip joint fluid itself (Engh et al., 2009). The increased levels of cobalt have been suggested as the potential cause for hypersensitivity reactions reported in these patients. Coating the metal bearing surfaces has been suggested to reduce wear and ion release with chromium nitride coatings showing the greatest level of interest (Fisher et al., 2002). However, many coatings have reported unsatisfactory *in vitro* results often due to delamination of the coating (Leslie et al., 2013).

When work for this thesis began in 2010, issues relating to early failure of metal-on-metal were only attributed to the recalled ASR design (Cohen, 2011, Langton et al., 2010). Work focussing on the application for novel coatings in a metal-on-metal system ("SMART HIP" Project Number TP-Q0033F, funded by the UK TSB) was, therefore, still clinically relevant. Silver chromium nitride coatings in this project were proposed to offer a potential benefit in the release of anti-microbial silver (Royle, 2012). Low (17 wt%) silver containing coatings, however, were shown to fail while higher (51 wt%) bulk silver containing coatings have shown resistance to subluxation damage (Royle, 2012) although these had not been widely tested under aggressive test methodologies. In the 8th annual report from the England, Wales and Northern Ireland National Joint Registry (2011), higher revision rates were observed in the entire metal-on-metal population, not just the ASR, compared to other bearing combinations which rapidly led to the decline of this bearing combination.

Although currently no work has reported cobalt release in metal-on-polyethylene bearings, retrievals have shown scratching of the head (Tipper et al., 2000) and there have been reports of pseudotumours and increased blood cobalt levels in patients receiving metal-on-polyethylene hip replacements (Walsh et al., 2012, Savarino et al., 2002). Polyethylene wear has predominantly been believed to be the limiting factor in the lifetime of this bearing combination. Wear reduction has focused on crosslinking the material (Muratoglu et al., 1999) and the adoption of ceramics both bulk and in coating form (Wang and Essner, 2001, Galvin et al., 2008) leading to some studies reporting revision due to polyethylene wear only in conventional polyethylene (Kurtz et al., 2013). The potential for ceramic coatings has therefore been proposed to not only reduce polyethylene wear but prevent cobalt release in this bearing combination as well (UK TSB funded project “BERTI” Project Number 101005).

2 Literature Review

2.1 Total Hip Replacement

2.1.1 The Natural Hip Joint

The hip joint is a ball and socket synovial joint comprising of the head of the femur and the acetabulum of the pelvis, Figure 2:1 (Martini, 2007). In order to maintain stability of the joint, several ligaments form around the ball and socket creating an articular capsule. This is further reinforced by other ligaments including the iliofemoral and ischiofemoral ligaments as well as the muscles around the joint (Martini, 2007).

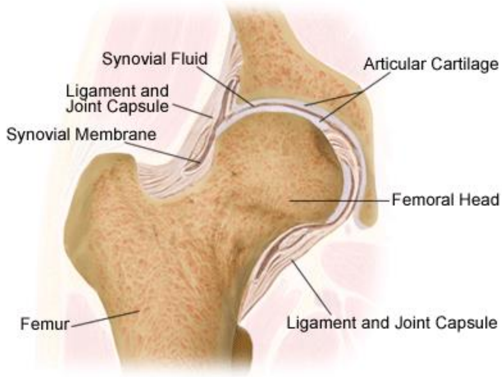


Figure 2:1: The hip joint showing the bones forming the joint and ligaments involved in stabilisation From: (Bahri Orthopaedics and Sports Medicine Clinic, 2012)

The primary roles of the hip joint are weight bearing and locomotion. The ability of the hip to allow for motion in flexion/extension, adduction/abduction and rotation can lead to the variety of movement seen in humans from walking to stair climbing (Callaghan et al., 2007). In order to perform these activities efficiently and without pain, the femoral head is covered in articular cartilage, a soft tissue which can allow for near frictionless movement (Erggelet and Mandelbaum, 2008). The inclusion of the synovial fluid in the joint provides a source of nutrition for the cartilage cells and allows for lubrication of the joint.

Healthy synovial joints can have a very low coefficient of friction suggesting favourable lubrication regimes (Nordin and Frankel, 2001).

The gradual degeneration of the cartilage due to aging or disease can lead to exposure of the underlying bone resulting in pain (Salter, 1998). Treatment options are initially conservative with changes in lifestyle and the use of non-steroidal anti-inflammatory drugs. However as the disease progresses, surgical interventions replacing the surfaces of hip joint are often the only option to allow for the restoration of quality of life through pain free mobility. The most common form of cartilage degeneration is osteoarthritis, estimated to affect approximately 8 million people within the UK (Doherty, 2012) which is the leading cause for primary hip replacement, Table 2:1. Other diseases which can also affect the hip joint are rheumatoid arthritis, affecting multiple joints and characterised by flare ups and remission (Cush et al., 2010), and avascular necrosis in which the femoral head is damaged by a loss of blood supply.

Table 2:1: Summary of indications leading to primary hip replacement procedures in the UK in 2012 based on work published by the UK National Joint registry (2013)

Indication	Percentage of patients
Osteoarthritis	92
Avascular necrosis	2
Fracture of the femoral neck	3
Congenital dislocation/dysplasia of the hip	1
Inflammatory arthropathy	<1
Failed hemoarthoplasty	1
Trauma - chronic	1
Previous surgery – non trauma related	<1
Previous arthrodesis	<1
Previous infection	<1
Other	1

2.1.2 History and Development of Total Hip Replacement

The need to produce an effective alternative bearing surface to replace the natural head and cup of the hip joint has been recognised for over a century. The first report of a hip replacement was performed in 1890 by Thomas Gluck, who used ivory and a grouting agent but reported problems with fixation (McKee, 1982). Interventions with different materials, particularly stainless steel, continued throughout the next fifty years but fixation and the biocompatibility of the artificial materials remained an issue (McKee, 1982, Wiles, 1958).

Sir John Charnley introduced the concept of the low friction arthroplasty in the 1960's utilising a polymer cup articulating against a metallic head. Although initially unsuccessful with a PTFE cup, the introduction of polyethylene provided better clinical results and still remains the gold standard in total hip replacement (Unsworth, 2006), Figure 2:2.

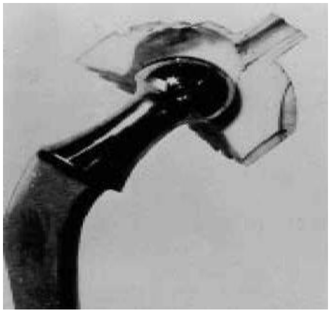


Figure 2:2: Early Charnley Low Friction THR comprising of a metal head and polymer cup (Dowson, 2001)

Despite this success, metal-on-polyethylene hip replacements have been limited in lifespan due to wear and the resulting immune response initiated by the body to the wear particles produced. This has led to research and the application of improved materials with the introduction of alternative bearing materials and combinations including ceramics, metals, coatings and alternative polymers

(Dowson, 2001). The majority of primary hip replacements implanted in the UK, however, are still the metal-on-polyethylene combination, Table 2:2. The mid-2000s saw an increase in the use of metal-on-metal bearings and a subsequent reduction in metal-on-polyethylene bearings implanted but recent concerns with these bearings has led to a marked reduction in metal-on-metal and a conversion to ceramic bearing surfaces.

Table 2:2: Trends in the use of different material combinations over the last 10 years in the UK based on work from the UK National Joint Registry (2013)

Material		Percentage of total primary hip replacements			
Head	**Cup**	**2003**	**2006**	**2009**	**2012**
Metal	Polyethylene	71	60	58	61
Metal	Metal	14	21	15	2
Metal	Ceramic	0	<1	1	<1
Ceramic	Polyethylene	11	9	10	16
Ceramic	Metal	0	<1	0	<1
Ceramic	Ceramic	4	9	16	21

2.1.3 Tribology

Understanding of the tribology of these implants is important as wear and the particles produced by the bearing surfaces can limit the long term success of an artificial joint. Tribology is the study of two surfaces moving relative to each other encompassing friction, lubrication and wear (Affatato et al., 2008b). At a microscopic level surfaces are uneven and as two surfaces move relative to each other the asperities on the surfaces interact. Removal of material is referred to as wear and the amount of this that occurs is often linked to the friction and lubrication of the surfaces (Bhushan, 2002). In a healthy hip joint, the synovial fluid and articular cartilage provide an incredibly effective system with minimal wear occurring over the 80+ years of use. In an artificially replaced hip joint, this ideal condition is not always possible to replicate and greater wear is normally produced (Callaghan et al., 2007).

Friction and Lubrication

Friction is the resistance of one surface against another, dependent on the load applied (Wen and Huang, 2012). Lubrication is a process which can reduce wear and friction by acting as a barrier between the two surfaces, often carrying some of the load exerted (Callaghan et al., 2007). Lubrication can occurs in three main forms: boundary, mixed or fluid film, Figure 2:3. In boundary lubrication, the fluid is not thick enough to prevent contact between the two surfaces and so asperity contact occurs. In fluid film lubrication, the surfaces are fully separated by the lubricant allowing for smoother motion and reduced wear. Mixed lubrication is a form in which both types of lubrication occur.

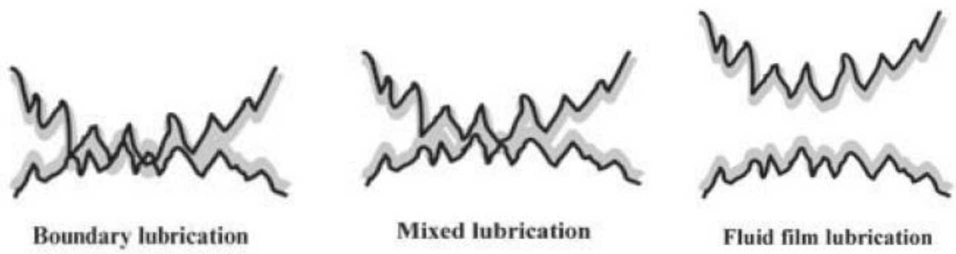


Figure 2:3: Diagram showing the three main lubrication regimes (Dowson and Jin, 2006)

There are several tribological theories which aim to predict the lubrication regime in a particular system. A Stribeck curve is well documented in use in tribological systems including hip replacements. This curve plots the coefficient of friction, f, against the Sommerfeld number, Z; a function of load, P, viscosity, η, and entraining velocity, U, as well as femoral head radius, R, shown in equation 1 (Scholes and Unsworth, 2000).

$$z = \frac{\eta U R}{P} \qquad (1)$$

The Stribeck curve shows an initial high friction coefficient when the Sommerfeld number is low relating to low viscosity, slow speed, small radius or high load, representing boundary lubrication, Figure 2:4. As the Sommerfeld number increases, the coefficient of friction decreases and a mixed lubrication regime is experienced until this eventually produces fluid film lubrication with a low coefficient of friction. The coefficient of friction increases past this point as the fluid itself, with increasing thickness, introduces additional friction into the system (Smith et al., 2001).

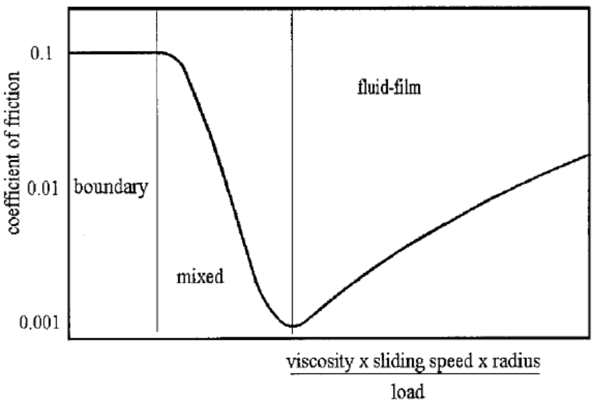


Figure 2:4: An idealised Stribeck curve showing the three forms of lubrication in relation to friction and other parameters (Smith et al., 2001)

In 1978, Hamrock and Dowson developed a formula to determine the minimum film thickness, h_{min}, of lubricant also based on the load, velocity and radius size but specific to material used with the Young's modulus of the bearing material, *E'*.

$$h_{min} = 2.8R\left(\frac{\eta U}{E'R}\right)^{0.65}\left(\frac{P}{E'R^2}\right)^{-0.21} \quad (2)$$

The minimum film thickness can describe the distance between the two surfaces and thus, the lubrication regime can be predicted with the surface roughness of the bearing surfaces. The mean surface roughness, Ra, can be used to provide a value known as the lambda ratio, λ (equation 3).

$$\lambda = \frac{h_{min}}{Ra} = \frac{h_{min}}{\sqrt{R^2_{a\,(head)} + R^2_{a\,(cup)}}} \quad (3)$$

A large lambda ratio implies greater separation between the two surfaces with a thicker lubricant or smoother surfaces, indicating improved lubrication and less asperity contact. A value of 3 or greater implies fluid film lubrication and complete separation of the surfaces. A lambda ratio below 1 suggests poor lubrication in the form of boundary lubrication resulting in contact between the surfaces while a value between these values denotes mixed lubrication.

Wear

When asperity contact occurs, material from these surfaces can be removed referred to as wear. A number of wear mechanisms can occur either due to mechanical or chemical interactions. These are generally divided into the mechanisms of abrasive, adhesive, fatigue and corrosive wear, Figure 2:5.

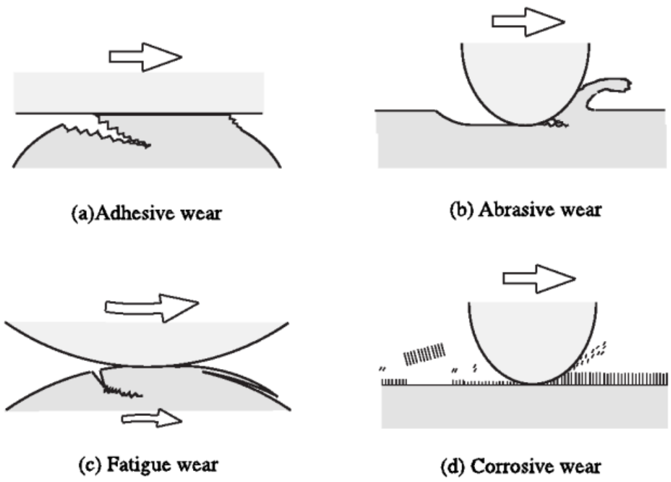


Figure 2:5: Schematic showing four main wear mechanisms (Bhushan, 2010)

Abrasive wear is perhaps the most commonly considered wear mechanism. It involves the removal of the asperities in contact with another surface during rubbing of these two surfaces. This is often seen on the worn surface as ploughing with a groove developing where the material has been removed (Bhushan, 2010). Abrasion can occur as a two-body mechanism with the asperities on the bearing surface acting as the abrasives or as a third body mechanism with a particle interacting between the two surfaces (Wen and Huang, 2012). Abrasive wear is dependent on the hardness of the surface, the load and the sliding velocity.

Adhesive or sliding wear occurs when asperities on different surfaces become fused together and are removed due to their relative motion. This removal is often seen as flake-like sheets and can lead to crack initiation on the wear surface (Bhushan, 2010). In this wear mechanism, transfer of material from one surface to another can occur (Bhushan, 2010). The transferred material can release from the surface it is bound to, becoming a large wear particle. Adhesive wear between metal and polymer surfaces has been documented (Narayan, 2009) and it has been proposed that the wear rate in this combination, W, can be determined by the probability that contact will result in a wear particle, K, the load, P, and the hardness of the softer material, h, as described in equation 4 (Archard, 1953).

$$W = \frac{KP}{3h} \tag{4}$$

Fatigue wear is generated due to cyclic loading or repeated wear processes (Schmalzreid and Callaghan, 1999) and is, therefore, time dependent. This wear mechanism can lead to failure when the material's fatigue strength has been exceeded by the local stresses. The generation of small microcracks during this process can propagate over time resulting in fracture and wear debris (Narayan, 2009). Fatigue wear is dependent on the mechanical properties and strength of the substrate material (Wen and Huang, 2012).

Unlike the other wear mechanisms which are mechanical in nature, corrosion is a chemical form of wear which occurs when the surface atoms of a material react with a substance, usually liquid (Davis, 2001). This results in the degradation of the material and transfer of ions. In order for corrosion to occur, three things are required; an anode, a cathode and an electrolyte. Electrons flow from the anode to the cathode via the electrolyte or conducting media. Although corrosion can occur in polymers and ceramics, it is most commonly associated in metals (Yan et al., 2006a). In orthopaedic CoCrMo metals, corrosion is considered to be reduced due to the production of a passive chromium oxide film on the surface of the implant (Yan et al., 2006b). While this film can prevent corrosion, the motion between the bearing surfaces can damage or remove it increasing the rate of corrosion (Yan et al., 2006b); this process of wear and corrosion is referred to as tribocorrosion (Yan et al., 2006a).

2.1.4 Wear of Hip Replacements

Clinical Wear Modes

McKellop (2007) proposed 4 clinical modes of wear of hip replacements, Figure 2:6. Mode 1 refers to a wear condition in which the bearings surfaces articulate against each other as designed. Mode 2 represents edge loading of the head articulating against rim of the cup which has been recognised in retrievals of metal-on-metal bearings (Matthies et al., 2011a) and hypothesised as the cause for stripe wear observed in heads of ceramic-on-ceramic retrievals (Walter et al., 2004). Mode 3 signifies abrasive wear generated due to the presence of third body particles, often bone, bone cement or metal debris believed to be the cause of scratches seen on the femoral heads of retrieved metal-on-polyethylene bearings (Tipper et al., 2000). Mode 4, divided into 4A and 4B, represents wear generated from two non-bearing surfaces.

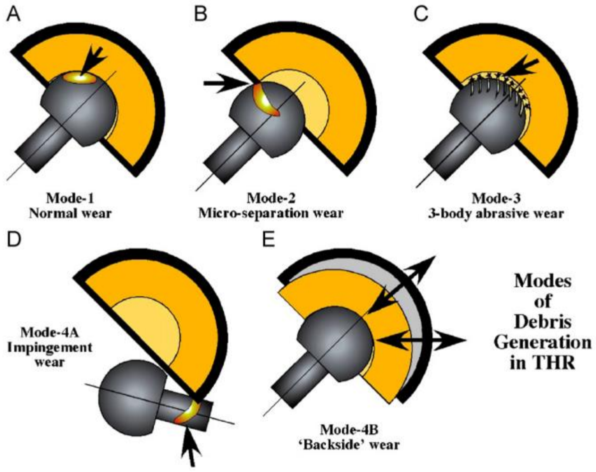


Figure 2:6: Four clinical wear modes in hip replacements as proposed by McKellop (2007)

Standardised Hip Simulator Testing

Wear screening devices have been used to evaluate materials in artificial hip replacements and vary from simplistic pin-on-disc tests to more complex physiological models such as hip simulators. These are important tools in the evaluation of material type and design used (Fisher, 2012). While simpler forms of wear testing can provide relatively quick results, they do not mimic the geometry of the bearings and so contact stresses and lubrication regimes do not represent the clinical condition (Affatato et al., 2008b). Improvements in the overall quality of hip replacements have increased the use of hip simulators to determine likely clinical success, replicating the normal biomechanical and kinematic conditions experienced *in vivo*. Although several different types of simulator exist, they can be split into two main categories: physiological and orbital. Physiological hip simulators utilise all degrees of freedom while orbital simulators focus on the rotation of the joint on a 23° cam, creating a biaxial rocking motion (Affatato et al., 2008b). However studies have shown comparable results.

In order to achieve consistency between different laboratories, a standardised test replicating the forces during walking is often adopted. In 2002, the first of three ISO standards was published specifying the speed, load and lubricant used in testing. Relating to tribological theory as presented in equation 2, section 2.1.3, increasing the speed and viscosity or reducing the load are predicted to increase the fluid film thickness and therefore reduce wear. Following ISO 14242-3 (2009), a double peaked load cycle with minimum and maximum loads of 300 N and 3000 N should be applied in an orbital hip simulator running at 1 Hz (60 rpm). One million cycles of this testing is considered equivalent to 1 year of walking, although this is possibly underestimated for an active population. Bovine serum is used as a lubricant as this has the appropriate viscosity (0.7-0.9 mPa s) and protein concentration (17 g/L) to correlate to synovial fluid (Mattei et al., 2011). Studies have shown that a reduction in protein concentration from 100% serum to 25% serum, and further to distilled water, decreases the friction factor for all materials combinations except metal-on-metal (Brockett et al., 2007). As seen in the Stribeck curve of Figure 2:4, a decrease in friction is associated with improved lubrication and should reduce wear. In the metal-on-metal case, the friction increases with decreasing protein concentration as these proteins adhere to the surface of the metallic components, decreasing the adhesive forces between the metallic bearings and acting as a solid lubricant (Wimmer et al., 2003). The protein concentration can, therefore, influence the wear of bearings and is important to produce clinically relevant wear rates (Clarke et al., 2001) with 25% diluted serum commonly used.

Adverse Hip Simulator Testing

Although hip simulators provide valuable insight into the wear behaviour of bearings, the standard test conditions provide an idealised condition replicating McKellop's (2007) wear mode 1. The continuous motion of the hip simulator can also lead to improved lubrication regimes and the positioning of these implants in the hip simulator can represent optimal placement while greater variation occurs clinically (Fisher, 2012). Similarly, the biomechanics occurring in the body are more varied and complicated than those produced in a standard hip simulator with various activities performed by patients.

In recent years, it has become necessary to further test the wear behaviour of an implant with the introduction of adverse testing. These test conditions are based on clinical modes of failure observed in retrievals which standard testing would not recognise (Langton et al., 2008) and therefore focus on the replication of McKellop's (2007) wear modes 2 and 3 as well as more extreme conditions of wear mode 1.

2.2 Polyethylene

2.2.1 Material Development

Polyethylene, comprised of covalently bonded carbon atoms attached to two hydrogen atoms has been widely used as the acetabular cup bearing surface in hip replacements since its introduction in the Charnley prosthesis. The ability of these carbon bonds to form short and long chains as well as attaching to a variety of other chemical groups allows for a variety of tensile strengths at a low cost (Peacock and Calhoun, 2006). In total hip replacements, ultra-high molecular weight polyethylene (UHMWPE) was found to produce lower levels of wear compared to other forms of polyethylene (Malhotra, 2012) and has been commonly used.

UHMWPE is a semi-crystalline polymer, comprising regions in which the carbon-carbon bonds of the molecule form an ordered, sheetlike structure, known as the crystalline lamellae (Kurtz, 2009). These are surrounded by disordered sections referred to as the amorphous region of the polymer (Kurtz, 2009). The extent of crystallinity in polyethylene is dependent on processing and generally ranges from 35-55% in orthopaedic devices (Callaghan, 2007). Increased crystallinity tends to produce a more brittle polymer (Callaghan, 2007) although it also produces greater wear resistance (Bruck et al., 2010).

The UHMWPE, machined and sterilised at a nominal radiation dose between 25-40 kGy, for use in hip replacements is referred to as conventional polyethylene in this thesis. This material has been shown to produce relatively large amounts of wear, so enhanced crosslinking normally using gamma radiation was introduced to reduce the wear (Kurtz, 2009). Gamma radiation exposure breaks the carbon-carbon bonds producing shorter polymer chains (Callaghan, 2007). Free radicals (unpaired electrons) are formed in this process which allow additional bonds between the carbon atoms of different chains to form, known as crosslinking (Oral et al., 2004). Free radicals generated in the amorphous region of the polyethylene tend to recombine to form crosslinks while those within the crystalline lamellae fail to recombine, forming alkyls, allyls and polyenyl, which remain trapped in the crystalline region of the material (Wolf et al., 2006). Irradiation in air, as historically performed to sterilise conventional polyethylene, has been reported to result in immediate oxidation of these free radicals which leads to material degradation (Tomita et al., 1999, Streicher, 1988); irradiation in inert atmospheres has therefore been recommended with most modern implants irradiated in this inert atmosphere (Muratoglu et al., 2003). Over the lifetime of the implant, however, the free radicals produced in the crosslinked polyethylene can react with diffused oxygen forming peroxy radicals which leads to the further generation of free radicals by reacting with the polyethylene chains. These second generation free radicals in turn react with oxygen which ultimately leads to oxidative embrittlement of the material and a degradation of mechanical properties (Oral et al., 2005). Post-irradiation melting has been performed to quench residual free radicals but this decreases the crystallinity of the material and therefore lowers the fatigue strength and wear properties of the polyethylene (Oral et al., 2004).

A recent alternative to reduce free radical content and prevent the degradation of material properties observed with a decrease in crystallinity has been to incorporate an anti-oxidant into the material, most commonly in the form of vitamin-E (α-tocopherol) (Tomita et al., 1999, Wolf et al., 2002, Oral et al., 2004). Two methods to include anti-oxidants into polyethylene have been reported. One blends the anti-oxidant into the polyethylene powder prior to shaping and irraditating the polymer (Oral et al., 2008) but this has been reported to decrease crosslinking efficiency when irradiated at cold temperatures due to the vitamin-E reacting with free radicals preventing the polyethylene from forming bonds. The other option is to diffuse anti-oxidant into the formed and irradiated cup. This does not influence the crosslinking efficiency but does limit the amount of free radicals which can be reduced (Oral et al., 2007).

Conventional and 75 kGy gamma irradiated polyethylene which has been thermally treated below the melt temperature and sterilised by gamma irradiation in nitrogen, have shown oxidation and a noticeable increase in wear when subjected to accelerated aging (Muratoglu et al., 2003). Vitamin-E has shown to be resistant to oxidation under accelerated aging and therefore no increase in wear has been reported in both blended and diffused forms (Lerf et al., 2013), (Shroeder and Durham, 2013). Real-time aging after 18 months has indicated that the blended vitamin-E polyethylene could be susceptible to very low levels of oxidation while vitamin-E diffused polyethylene has shown no oxidation (Rowell et al., 2011). More adverse methods of promoting oxidation have been developed using the organic compound squalene which can also show some oxidation in blended forms of the vitamin-E polyethylene (Wannomae et al., 2012)

2.2.2 Head Materials and Standard Simulator Wear

Wear of conventional polyethylene bearings has been reported to increase with diameter in retrieval studies of metal-on-polyethylene with wear rates of 25.9, 63.4, 75.6 and 88.7mm^3/year reported in 22, 26, 28 and 32 mm diameter bearings respectively (Kabo et al., 1993). This has also been shown in alumina-on-conventional polyethylene bearings tested under standard simulator conditions (Clarke et al., 1996), thereby limiting the diameter used to 36 mm. Despite this, conventional polyethylene bearings reported ten years survivorship of 98% (Crowther and Lachiewicz, 2002). According to the Australian Joint Registry (2013), the main reason for revision in these metal-on-polyethylene bearings is loosening/lysis with a cumulative incidence of revision of 4.2 % at 12 years. Larger (> 32 mm) diameter bearings have been reported to have higher revision rates than the smaller bearings possibly due to increased wear.

By crosslinking polyethylene through an increased irradiation doses lower wear rates have been produced. Polyethylene crosslinked at doses above 500 kGy however have displayed delamination and cracking damage (Oonishi et al., 2004). Therefore the majority of bearings currently are irradiated up to 105 kGy, Table 2:3. As the material has demonstrated lower wear rates, this has suggested that increased diameters up to 52 mm could be adopted; these have been tested experimentally. The increased diameter theoretically allows for increased range of motion and decreased risk of dislocation clinically (Burroughs et al., 2005). However, an increased diameter also results in a decreased liner thickness which in turn increases the stresses within the material (Oonishi et al., 1998). Some studies have shown that increased liner thickness reduces wear (Oonishi et al., 1998, Johnson et al., 2014) whilst others have suggested increasing wear with increased thickness (Shen et al., 2011). The differences in wear in either case is small. Wear of metal-on-crosslinked polyethylene has been reported to be independent of diameter (Herrera et al., 2007, Muratoglu et al., 2001) possibly due to difficulties in measuring the very low amount of wear produced. However, ceramic-on-crosslinked polyethylene has suggested increasing polyethylene wear with diameter (Zietz et al., 2013).

Table 2:3: Wear rates of metal-on-polyethylene under standard simulator conditions

Irradiation dose, kGy	Diameter, mm	Mean wear rate, mm^3/mc	Study
25-40	28	10 ± 4	Galvin et al. (2008)
		10.1 ± 0.8	Bragdon et al. (2003)
		11.8 ± 2.9	Shorez et al. (2008)
		11.9	Saikko et al. (2002)
		15.2 ± 1.4	Spinelli et al. (2010)
		16.0 ± 1.7	D'Lima et al. (2003)
		18	Taddei et al. (2011)
		21.9 ± 3.3	Saikko & Shen (2010)
		23.6 ± 7.8	Weimin et al. (2009)
		27	Taddei et al. (2011)
		30.3 ± 1.7	Shen et al. (2011)
		34	Affatato et al. (2000)
		35 ± 10	Fisher et al (2006)
		37.2	Elfick et al. (2001)
		37.7	Liao & Hanes (2006)
		38	Taddei et al. (2011)
		39	Kang et al. (2008)
		47 ± 5	Barbour et al. (2000)
		51 ± 11	Essner et al. (2005)
		51.7 ± 1.2	Smith & Unsworth (2000)
		62	Taddei et al. (2008)
		68	Gonzalez-Mora et al. (2009)
		70 ± 10	Jedenmaln et al. (2009)
		172	Affatato et al. (2011)
	32	46 ± 8.7	Herrera et al. (2007)
		75	Wang & Essner (2001)
		156.7	Sorimachi et al. (2009)
		178 ± 23	Kubo et al. (2009)
	36	20.0 ± 1.3	Saikko & Shen (2010)
		25.2	Kelly et al. (2010)
		31.6 ± 1.9	Shen et al. (2011)
50	28	7.4 ± 0.9	Shen et al.(2011)
		9.2	Liao & Hanes (2006)
		22	Bowsher & Shelton (2001)
	36	7.8 ± 1.5	Shen et al.(2011)
75	28	1.5 ± 1.2	D'Lima et al. (2003)
		8	Galvin et al.(2007)
	44	13.4	Sorimachi et al.(2009)
		31 ± 17	Kubo et al. (2009)
90	28	1.3 ± 0.8	Loving et al.(2013)
	32	1.35 ± 0.68	Herrera et al. (2007)
	36	1.2	Kelly et al. (2010)
		2.5 ± 1.1	Johnson et al.(2014)
	44	0.2 ± 0.2	Herrera et al. (2007)
	48	9.8 ± 4.0	Loving et al.(2013)
	52	4.8 ± 3.1	Herrera et al. (2007)
95	36	10.4 ± 1.6	Galvin et al. (2010)
100	28	3	Kang et al. (2008)
		9	Taddei et al. (2011)
		12.4	Roy et al.(2011)
	36	10.6 ± 1.4	Fisher et al. (2006)
105	32	5.62 ± 3.5	Essner et al. (2005)
		6.19 ± 4.43	Wang & Schmidig (2003)

Crosslinked polyethylene has been used increasingly over the last 10 years in the place of conventional polyethylene due to the improved wear resistance achieved, with more metal-on-polyethylene bearings utilising a crosslinked polyethylene than conventional according to the Swedish Joint Registry (2012). Low clinical penetration rates of polyethylene irradiated at 100 kGy after 3 years were reported as 0.23 mm (Digas et al., 2004). In polyethylene receiving similar doses of radiation, annual wear rates in some instances have been reported as low as 20 μm per year, with revision after 16.5 years only 4% (Harris and Muratoglu, 2005). This has resulted in a decreased incidence of revision for loosening and lysis of 1.5 % after 12 years (Graves, 2013). Despite the decreased revision rates, cases of oxidation in retrieved crosslinked polyethylene have been reported (Wannomae et al., 2006, Currier et al., 2010).

The inclusion of vitamin-E in crosslinked polyethylene has been reported to produce low wear rates in simulator studies, Table 2:4. Affatato et al., (2011), however, found wear increasing two fold with the introduction of 0.1 wt% vitamin-E into 28 mm liners irradiated at 70 kGy compared to liners irradiated at the same dose due to a reduction in the crosslink density. This highlights the necessity to maintain comparable crosslink density in the polyethylene and therefore, higher irradiation doses are required in the blended forms in order to achieve low wear. When this is achieved, wear rates between 1 and 2 mm^3/mc have been reported in bearings of 36 and 40 mm diameter (Oral 2006a, Traynor 2011). Anti-oxidant incorporated bearings have only been implanted over the last 5 years and therefore, there are currently few clinical results, however these trials are underway (van den Veen et al., 2012). Current retrieval analysis after a mean of 0.8 ± 0.8 years has shown the predominant reason for revision to be instability of the replacement (Kurtz et al., 2013) however, these are based on a small number of retrievals after a short implant duration. Biological tests conducted on the vitamin-E stabilised polyethylene particles have suggested that vitamin-E may behave as an anti-inflammatory agent, possibly reducing the risk of osteolysis in these bearings (Bladen et al., 2013).

Table 2:4: Wear rates produced by metal- on -vitamin-E substituted crosslinked polyethylene

Anti-oxidant incorporation method	Diameter, mm	Irradiation dose, kGy	Wear rate, mm^3/mc	Study
Diffused	28	85-100	0.83 ± 0.30	Oral et al. (2006)
	36	85-100	1.03 ± 0.52	Oral et al. (2006)
	44	85-100	5.96	Shroeder & Durham (2013)
Blended	28	70	137	Affatato et al. (2011)
	28	91	6.1	Lerf et al. (2013)
	40	120	1.81 ± 0.90	Traynor et al. (2011)

The polyethylene cup has been paired with a variety of different ceramic and metal head materials (Wang and Essner, 2001). Although Charnley originally utilised a metal head and the use of CoCrMo metal-on-polyethylene remains popular (Powers-Freeling, 2013), ceramics have been proposed due to their increased scratch resistance with alumina, zirconia and zirconia toughened alumina (ZTA) reported articulating against polyethylene (Zietz et al., 2013). Historically, concern over the use of ceramics has primarily focussed on the potential to fracture, given the brittle nature of the material (Cai and Yan, 2010) but the incidence of this has reduced with improvements in manufacturing resulting in the average grain size of currently generation ceramics reduced from that of the first generation material; 1.8 μm compared to 3.2 μm respectively (Cai and Yan, 2010). Zirconia can undergo phase transformation leading to fracture and therefore alumina is the preferred ceramic despite producing a higher wear rate (Lee and Kim, 2010).

One limitation of ceramic-on-polyethylene bearings are the diameter to which the heads can be safely manufactured (Rodriguez and Cooper, 2013). An alternative to the use of bulk ceramic heads is to coat a metallic head with a ceramic coating allowing larger diameters to be considered. The use of surface coatings to minimise friction and wear has been established in other engineering systems such as in cutting and forming tools (Grischke et al., 1995) and in gas turbine engines (Padture et al., 2002). In hip replacements, several coating methods have been investigated such as physical vapour deposition (PVD), chemical vapour deposition (CVD) and sputtering to produce chromium nitride, carbon chromium nitride, titanium nitride and diamond-like carbon (Galvin et al., 2008). In addition oxidising the surface of a zirconium alloy with oxygen to produce a zirconia surface known as Oxinium (Garvin et al., 2009) has been performed although this may be considered slightly differently to a coating. It has been widely recognised that the good adhesion between the substrate and coating is required to prevent failure (Holmberg and Matthews, 2009).

The use of ceramic heads has been less popular than metal heads with approximately 10,000 ceramic-on-polyethylene procedures reported in the UK in 2012 compared to approximately 45,000 metal-on-polyethylene procedures (Powers-Freeling, 2013). Ceramic-on-polyethylene bearings have been implanted in younger patients (mean age of 50.2 years) compared to metal-on-polyethylene bearings (mean ages 63.9 years) (Callaghan and Liu, 2009) yet, revision rates for ceramic-on-polyethylene are comparable to those of metal-on-crosslinked polyethylene showing a revision rate of 5.6 % after 12 years (Graves, 2013). The use of ceramics coatings clinically has been low, but reports of adhesive failure as early as 1 year after implantation in titanium nitride coatings raised concerns (Harman et al., 1997). Retrieved DLC coatings have also shown small pit formation and mechanical failure on the heads leading to a failure rate of 45 % after 8.1 years (Taeger et al., 2004).

Ceramic-on-polyethylene bearings have shown to produce wear rates comparable or lower than metal-on-polyethylene under standard conditions, Figure 2:7. Several ceramic coatings have been investigated, Table 2:5, with mixed results as some PVD titanium nitride and CVD diamond-like carbon coatings reporting wear reduction from metal-on-polyethylene (Pappas et al., 1995, Affatato et al., 2000) while the majority of coatings reporting no improvement in polyethylene wear rate (Liu et al., 2012, Saikko et al., 2001, Galvin et al., 2008). This is attributed to the coating method producing little improvement in surface roughness with Rt and Rp parameters reported to correlate to polyethylene wear rates (Galvin et al., 2008). A CoCrMo coating on itself produced via a PVD process reported an increased Ra surface roughness from 0.05 to 0.1 μm, yet polyethylene wear was decreased and fewer scratches were observed on the liners paired with these coated heads (González-Mora et al., 2009) suggesting that Ra has little influence on polyethylene wear and other surface roughness parameters may be more influential .

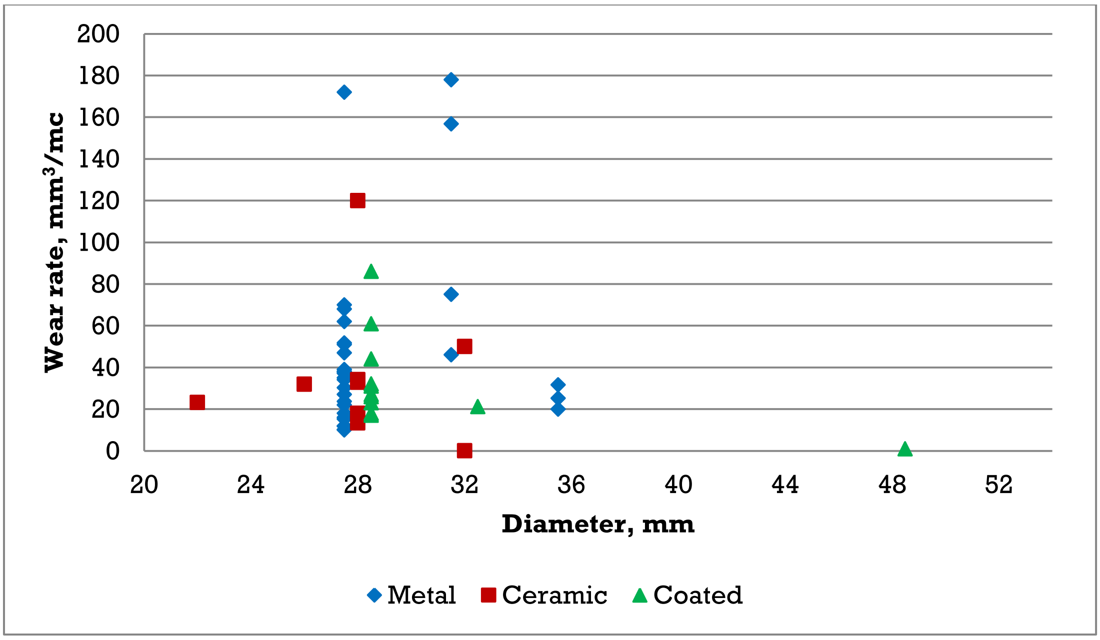


Figure 2:7: Wear rates of conventional polyethylene under standard simulator conditions showing little difference with different head materials

Table 2:5: Summary of coated metal-on-polyethylene testing under standard hip simulator conditions

Surface coating	Method of coating	Diameter, mm	Polyethylene wear rate, mm^3/mc	Study
TiN	AEPVD	28	18 ± 8	Galvin et al. (2008)
TiN	PVD	32	21.2	Pappas et al. (1995)
TiN	PVD	48	1	Pappas et al. (1995)
DLC	PACVD	28	31 ± 2	Galvin et al. (2008)
DLC	FCVA	28	86	Liu et al. (2012)
DLC	CVD	28	26	Affatato et al. (2000)
DLC	P/CVD	28	60.9 ± 5.8	Saikko et al. (2001)
Graphit-iC™	-	28	23 ± 10	Galvin et al. (2008)
CoCrMo	PVD	28	44	González Mora et al. (2009)
CrN	AEPVD	28	17 ± 2	Galvin et al. (2008)
CrN	AEPVD	28	27 ± 10	Galvin et al. (2005)
CrN	Sputter	28	32 ± 27	Galvin et al. (2008)

2.2.3 Adverse Wear Conditions

In metal-on-polyethylene retrievals, macroscopic and microscopic scratches have been observed on the femoral heads which increase the surface roughness of the bearing surface to a maximum reported surface roughness, Ra, of 4.3 μm (Tipper et al., 2000), although other retrieval studies have reported lower Ra values of 0.17 μm in metallic heads after a similar implant life (Haraguchi et al., 2001), Table 2:6. The damage created in these retrieved heads has been observed as localised with some retrieved heads showing more damaged regions than others (Tipper et al., 2000). Wear debris and particulates created during implantation such as bone cement and bone may be trapped within the joint capsule and synovial fluid in patients acting as third body abrasives and creating scratching on the bearing surfaces leading to Mode 3 wear (McKellop, 2007). These particles can also embed themselves into the articulating surface (Wang and Essner, 2001) which can continue to act as an abrasive against the opposite bearing surface.

Table 2:6: Summary of surface roughness of heads retrieved from metal-on-polyethylene bearings

Mean Ra ± sd (range), μm	Mean Rp ± sd (range), μm	Mean Rt ± sd (range), μm	Study
0.02 ± 0.005	0.07 ± 0.02		Tipper et al. (2000) Low damage bearings
0.74 ± 0.89 (0.01-4.30)	1.54 ± 0.97		Tipper et al. (2000) High damage bearings
(0.013-0.037)		(0.041-0.086)	Raimondi et al.. (2001)
(0.04 -0.12)			Haraguchi et al. (2001) Müller bearings
0.17 ± 0.32 (0.04-1.52)			Haraguchi et al. (2001) Charnley bearings
	(0.068-0.400)		Minakawa et al. (1998)
		0.1-2.0 scratches	Jasty et al. (1994)
0.062 (0.041-0.080)	0.240 (0.2-0.39)	1.08 (0.82-1.55)	Hall et al. (1997)
0.023 ± 0.015			Kusaba & Kuroki (1997)
0.01-4.20			Kruger et al. (2013)
0.012 ± 0.0002			Eberhardt et al. (2009)
0.010 ± 0.008			Elfick et al, (1999)
0.12 ± 0.11 (0.01-0.45)	1.00 ± 0.77 (0.07-3.46)		Ito et al.(2010)
(0.025-0.11)	(0.8-1.2)	(1.5-2.0)	Patten et al. (2010)

To replicate the abrasion occurring clinically, two adverse test conditions exist: the addition of third body particles to the test fluid or direct scratching in a controlled manner. Third body particles used include alumina, bone cement, CoCrMo (Bragdon et al., 2004) as well as titanium (Ti6Al4V) (Halim et al., 2014) at varying concentrations. Similarly, direct damage to the heads has been generated through various methodologies, Table 2:7. The use of a diamond stylus is a popular method generating distinct scratches (Barbour et al., 2000, Galvin et al., 2005, Lee et al., 2009), but the load at which scratching is applied varies. An increase in load affects the peak height, Rp, measured on the heads. The number of scratches generated can also differ with different patterns reported in the literature (Barbour et al., 2000, Affatato et al., 2005, Lee et al., 2009). Other methods of damage include the use of CoCrMo bead embedded in UHMWPE and used to scratch a head at 80 N (Barbour et al., 2000). Less controlled, overall head damage using SiC grit paper (Bowsher and Shelton, 2001) or blasting with glass beads (Bowsher et al., 2008) has also been performed creating greater roughnesses, closer to that reported in bearings tested with third body particles added to the test fluid.

Table 2:7: Influence of the method of head damage on the Ra and Rp on metal heads

Method of damage	**Mean Ra (range), μm**	**Study**
Diamond stylus at 2.5 N	0.035 ± 0.019	Barbour et al., (2000)
CoCrMo bead at 80 N	0.017 ± 0.004	Barbour et al., (2000)
SiC grit paper	(0.2-0.622)	Bowsher and Shelton (2001)
Pressurized blasting with glass bead	(0.475-0.643)	Bowsher et al (2008)
Alumina third body particles	0.62	Muratoglu et al., (2000)
Bone cement third body particles	0.11	Muratoglu et al., (2000)

Direct roughening of the femoral head is most commonly achieved using a diamond stylus (Barbour et al., 2000, Lee et al., 2009, Galvin et al., 2005). This has produced greater wear rates than an embedded CoCrMo bead, increasing wear in metal-on-conventional polyethylene bearings from 47 ± 5 mm^3/mc under standard conditions to 55 and 112 mm^3/mc in CoCrMo bead and diamond stylus damaged pairs respectively (Barbour et al., 2000). Diamond stylus roughening at a force of 30 N has also produced increased wear rates of 19.6 mm^3/mc in metal-on- 90 kGy crosslinked polyethylene (Lee et al., 2009). Alumina heads have shown increased resistance to diamond stylus damage applied at 1.5 N with a small wear reduction from 18 mm^3/mc in standard testing to 12 mm^3/mc (Galvin et al., 2005). Similar damage applied at a higher load of 30 N to a greater area of 28 mm diameter ZTA head has reported similar effects against highly crosslinked polyethylene (Lee et al., 2009).

The area of damage generated has been proposed to be more influential to wear than the roughness achieved (Bowsher et al., 2008) with increased wear rates in metal-on-conventional and 50 kGy irradiated polyethylene when the metal surface is scratched using SiC grit paper (Jedenmalm et al., 2009, Bowsher and Shelton, 2001). A higher wear rate of 140 ± 60 mm^3/mc in the conventional polyethylene bearings (Jedenmalm et al., 2009) was comparable to 28 mm diameter conventional polyethylene against explanted heads ranging from 103.7 to 149.5 mm^3/mc (Elfick et al., 2001).

Instead of directly roughening the head counterface, third body particles have also been added to the test fluid to act as abrasives. Chromium, bone cement, alumina and titanium particles has all be utilised (Bragdon et al., 2004, Lerf et al., 2013). Chromium particles added to the test fluid at a concentration of 0.125

mg/mL have shown to have little influence on conventional polyethylene wear (Bragdon et al., 2004). Similarly bone cement has only been reported to increase conventional wear rates at concentrations above 5 mg/mL (Wang and Essner, 2001). The addition of barium sulphate in bone cement is the critical component leading to increases in wear (Bragdon et al., 2004). The removal of bone cement particles and further "clean" testing has shown a reduction in the wear rates of conventional polyethylene to levels at or below standard wear rates. Indeed, Sorimachi et al. (2009) reported a threefold reduction in wear following the removal of bone cement particles in 32 mm diameter bearings compared to the initial standard test conditions before the addition of bone cement particles. Bone cement abrasives have not produced changes to the surface roughness of the metal head but have adhered to both bearing surfaces, possibly preventing additional surface damage to the polyethylene with the bone cement contacting the heads instead.

The utilisation of a ceramic head has shown wear reduction in third body test conditions utilising bone cement at concentrations from 1 to 10 mg/mL, failing to produce increased conventional polyethylene wear (Wang and Essner, 2001), Table 2:8. Bone cement does not scratch or adhere to the ceramic surfaces as it does with metal bearing surfaces (Wang and Essner, 2001) thereby preventing any changes to wear when these particles are removed from the test fluid.

Table 2:8: Wear rates of 32 mm diameter ceramic on polyethylene bearings under third body bone cement conditions showing little to no increase in wear compared to standard conditions

Concentration, mg/mL	Polyethylene type	Head	Wear rate, mm^3/mc	Increase in wear rate	Study
1	Conventional	Alumina	60	-20	Wang and Essner (2001)
1	Conventional	Zirconia	22	-56	Wang and Essner (2001)
5	Conventional	Alumina	50	-33	Wang and Essner (2001)
5	Highly crosslinked	Alumina	37.33	349	Wang and Schmidig (2003)
5	Highly crosslinked	Alumina	18	-42	Kubo et al., (2009)
5	Conventional	Zirconia	35	-30	Wang and Essner (2001)
5	Highly crosslinked	Zirconia	30	24900	Wang and Schmidig (2003)
10	Conventional	Alumina	50	-33	Wang and Essner (2001)
10	Conventional	Zirconia	35	-30	Wang and Essner (2001)

Harder abrasives such as alumina have been reported to be more severe than bone cement tested at concentrations of 0.15 mg/mL with wear rates of 111 mm^3/mc in contrast to 25 mm^3/mc (Bragdon et al., 2003). The effect of the damage produced by alumina third bodies with the removal of these particles, however, has not been fully investigated. Polyethylene crosslinked at 95 kGy has shown a reduction in wear rate compared to conventional polyethylene tested with alumina particles (Bragdon et al., 2004), but the percentage increase between standard and third body conditions could not be determined as wear in the crosslinked bearings was not measurable under standard conditions, Table 2:9. Vitamin-E blended highly crosslinked polyethylene however, has shown a fiftyfold increase in wear from standard conditions when alumina particles added a concentration of 0.15 mg/mL, increasing the wear rate to 97.4 ±25.9 mm^3/mc (Hinter et al., 2013).

Table 2:9: Increased wear rates in metal-on-polyethylene bearings under alumina third body conditions

Polyethylene	Concentration, mg/mL	Diameter, mm	Wear rate, mm^3/mc	Study
Conventional	0.15	28	111	Bragdon et al., (2003)
	0.15	32	168	Bragdon et al., (2004)
Crosslinked	0.15	32	48	Bragdon et al. (2004)
	0.15	28	39	Bragdon et al. (2003)
	0.3	32	121	Bragdon et al. (2004)
Vitamin-E Crosslinked	0.15	40	97.4	Hinter et al., (2013)

Other test conditions including changing the loading of the polyethylene shown little change in conventional polyethylene wear (Smith and Unsworth, 2000). Simulated jogging and stumbling tests on moderately crosslinked (50 kGy) polyethylene showed no significant change in polyethylene wear (Bowsher and Shelton, 2001). Increasing speed in walking and jogging, however, increased wear to 52 mm^3/mc during walking and 35 mm^3/mc during jogging (Bowsher and Shelton, 2001). Polyethylene has also been shown to be resistant to edge loading conditions; lateralisation conditions in metal-on-50 kGy irradiated polyethylene bearings produced wear rates of 32.2 mm^3/mc (Bowsher et al., 2008) and showed reduction in the wear rates of alumina-on-conventional polyethylene from 25.6 ± 5.3 mm^3/mc under standard conditions to 5.6 ± 4.2 mm^3/mc with lateralisation (Williams et al., 2003). High angle tests have reported decreasing wear with increasing inclination angles from 24.2 ± 1.0 (at 40° to the horizontal plane) to 16.3 ± 0.7 mm^3/mc (at 70° to the horizontal plane) (Lancin et al., 2007). This reduction has also been reported in crosslinked and vitamin-E blended highly crosslinked polyethylene producing wear rates of 17 and 21 mm^3/mc (Saikko and Shen, 2010, Lerf et al., 2013).

The introduction of head roughening in combination with lateralisation and severe activity, however, has shown significant wear increases. The wear rate under lateralisation conditions has been reported to increase from 32.2 mm^3/mc under smooth conditions to 290.8 mm^3/mc in 50 kGy irradiated polyethylene combined with a roughened head (Bowsher et al., 2008). Similarly, jogging activities with roughened heads have shown increased wear rates compared to smooth jogging conditions (Bowsher and Shelton, 2001). This was most dramatic in fast (1.75 Hz) jogging where the wear rate increased by 89 times to 3123 mm^3/mc, a fifteenfold increase from similarly roughened walking conditions.

2.3 Metal-on-Metal

2.3.1 First Generation and Improvements in Manufacture

An alternative bearing combination to metal-on-polyethylene bearings is the substitution of the polymer cup with a metallic cup. The metal used as a bearing surface is a cobalt chromium molybdenum alloy (CoCrMo) which has shown to perform well in the body and lead to a low incidence of osteolytic immune responses (Dumbleton and Manley, 2005). Early metal-on-metal (MoM) bearings used in the 1960s reported several failures attributed to the poor manufacturing and tolerances (Dehn, 2005). However, long term studies showed that those MoM implants which did not fail early had high survival percentages past 10 years (Dumbleton and Manley, 2005). For instance, the first generation McKee-Farrar MoM implant was reported to exhibit 84.75% survival at 13 years and

81.8% after 28 years in patients with rheumatoid arthritis (August et al., 1986, Brown et al., 2002).

The microstructure of the CoCrMo can exist in several forms dependent on the carbon content and method of manufacture. Bearings are required by ASTM F75 (2012) to contain chromium and molybdenum at 27-30 % (mass/mass) and 5-7% respectively, balanced to cobalt. These metals can consist of low carbon (less that 0.14%) and high carbon (0.15-0.35%) using ASTM F1537 (2011). Reports from simulator testing have shown high carbon bearings to perform better than low carbon bearings (Isaac et al., 2006, Wang et al., 1999).

Metal bearings are manufactured either as-cast or wrought. Although the cast metal tends to show larger grains and "blocky" carbides in comparison to the smaller grains of the wrought CoCrMo, little difference in wear has been observed (Dowson et al., 2004b, Angadji et al., 2009). Similarly, under walking and jogging conditions, no significant difference in wear has been observed between as-cast and double heat treated metal-on-metal bearings in hip simulator studies (Bowsher et al., 2006b).

2.3.2 Design and Wear

Metal-on-metal bearings have been proposed due to the low wear volume compared to metal-on-polyethylene bearings (Dowson, 2001) with low steady state wear rates reported in metal-on-metal simulator studies, Table 2:10. The wear behaviour of metal-on-metal bearings has been extensively studied with reports of an initial high wear rate referred to as running or bedding-in (Anissian et al., 2001, Scholes and Unsworth, 2006) followed by a reduction in wear rate.

This wear pattern has been described as bi-phasic or tri-phasic with some observing a transition phase between run-in and steady state (Angadji et al., 2009, Royle, 2012). In the bi-phasic wear model, run-in occurs over the first million cycles (Scholes and Unsworth, 2006) whereas others have reported transition between 0.3 to 0.7 million cycles from the initial high run-in to steady state wear (Anissian et al., 2001). Other have reported a transitions phase from 0.33 to 1 million cycles (Royle, 2012). Therefore, it can be difficult to compare reported run-in wear rates and the degree to which the wear rate decreases from run-in to steady state is highly variable, reducing by as much as 25 times in one study (Barnes et al., 2008). In order to produce lower wear rates, it is hypothesized that larger diameter bearings promote fluid film lubrication and thus reduce wear as described in section 2.1.3. During the run-in phase, however, diameter has been shown to be less influential than clearance between bearings (Scholes and Unsworth, 2006). An optimal clearance between the head and cup is required to promote fluid film lubrication; various clearances have been used ranging from 20 μm to 240 μm. A small clearance of 50 μm has shown to promote enhanced lubrication and reduce run-in wear rather than larger clearances of 100 and 150 μm (Dowson, 2006).

Table 2:10: Summary of steady state MoM wear rates under standard condition showing a general trend of decreasing wear with increase diameter

Diameter, mm	Clearance, μm	Steady state wear rate, mm^3/mc	Study
28	56.3	0.45 ± 0.27	Goldsmith et al. (2000)
28	-	1 ± 0.4	Williams et al. (2007)
28	30	0.58 ± 0.03	Fisher et al. (2006)
28	30	0.1 ± 0.05	Fisher et al. (2006)
28	40-100	0.13	Wang et al. (1999)
28	96	1.00 ± 1.64	Anissian et al. (2001)
28	30	0.3	Williams et al. (2006)
28	-	1.48	Affatato et al. (2008a)
28	40-60	0.99	Al-Hajjar et al. (2013b)
28	40-100	0.12	Wang et al. (1999)
32	50-89	1.25	Ortega-Saenz et al. (2013)
32	56.4	0.77 ± 0.72	Ishida et al. (2009)
32	-	0.86	Affatato et al. (2008a)
36	-	0.915	Affatato et al. (2008a)
36	-	0.3 ± 0.6	Williams et al. (2007)
36	71	0.36 ± 0.62	Goldsmith et al. (2000)
36	40-60	0.35	Al-Hajjar et al. (2013b)
36	-	0.6 ± 0.18	Williams et al. (2013)
38	102-106	0.5	Alvarez-Vera et al. (2013)
39	-	0.3 ± 0.2	Leslie et al. (2009)
39	-	0.3	Fisher et al. (2006)
40	>100	0.41	Bowsher et al. (2006a)
40	>100	0.46	Bowsher et al. (2006a)
40	50-90	6.4 ± 10.6	Essner et al. (2005)
40	145-156	0.69 ± 0.52	Angadji et al. (2009)
48	153-157	0.26 ± 0.09	Royle (2012)
50	160-210	0.24	Vassiliou et al. (2006)
50	236-244	0.37	Li et al. (2011)
52	152-160	0.095	Saikko et al. (2013)
54	-	0.11 ± 0.07	Barnes et al. (2008)
55	-	0.13	Fisher et al. (2006)
60	234-240	0.35	Bowsher et al. (2009)
60	234-240	1.4	Bowsher et al. (2009)

As the run-in wear phase is generally short, steady state wear rates may be more relevant for long term implantation Steady state wear rates have shown an increase in diameter from 28 mm to 36 mm decreases wear from 0.45 ± 0.27 to 0.36 ± 0.62 mm^3/mc (Goldsmith et al., 2000). Diameter appears generally to be more influential in steady state wear reduction, with larger diameters producing less wear regardless of clearance, Figure 2:8. However, the steady state wear rates reported can significantly vary with the variability between bearings equal to or greater than the mean wear rate (Williams et al., 2006, Essner et al., 2005). Between tests, steady state wear rates as low as 0.11 mm^3/mc have been reported in 52 mm diameter metal-on-metal bearings (Barnes et al., 2008) yet higher wear rates of 6.4 mm^3/mc have also been reported under similar conditions (Essner et al., 2005).

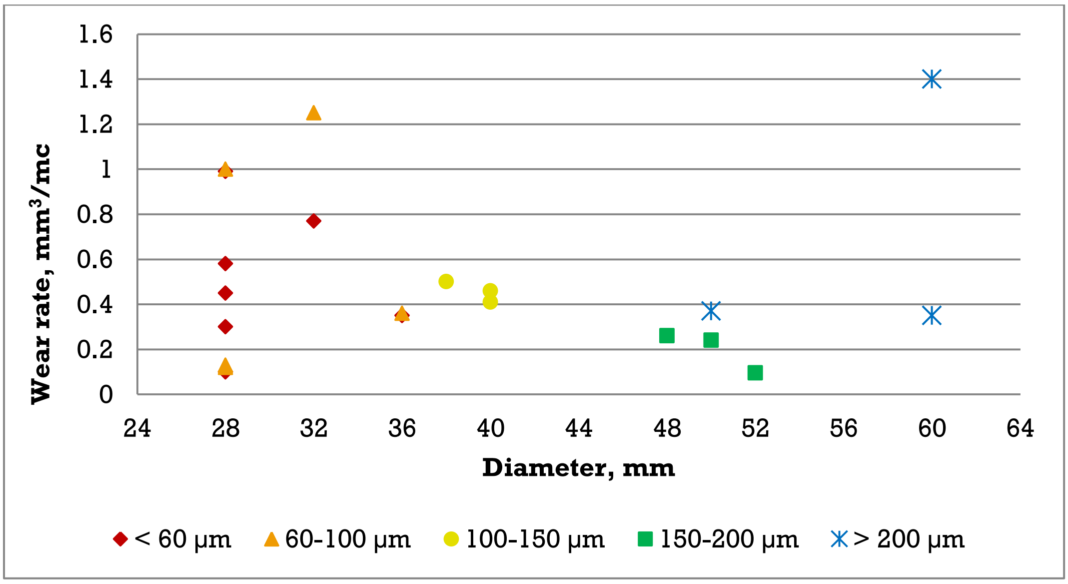


Figure 2:8: Diagram showing reported steady state wear rates in metal-on-metal bearings under standard conditions with different clearances influencing wear to a lesser extent than diameter

2.3.3 Adverse Wear Conditions

Metal-on-metal wear has been shown to be particularly sensitive to changes in loading and positioning during testing, Table 2:11. The swing phase load has been shown to influence wear decreasing the mean steady state wear rate from 0.3 mm^3/mc to 0.05 mm^3/mc with a reduction of load from 280 N to 100 N. The reduced wear rate was more pronounced in the initial run-in phase (Williams et al., 2006). This loading condition also altered the proportion of head wear, increasing from 60% to 75% with increasing load suggesting there may have been a change in wear mechanism. Wear was also reduced due to continuous motion with an increased wear rate observed when a novel protocol of 10 minute walking followed by stopping for 1 minute was implemented (Roter et al., 2002). Increasing both the frequency and loading by introducing jogging has also been investigated with a run-in wear rate of 3 to 4 mm^3/mc reported, double that of standard walking (Bowsher et al., 2006a).

Table 2:11: Summary of adverse tests conducted on MoM bearings and the resulting increase in wear rate

Test condition	Diameter, mm	Steady state wear rate, mm^3/mc	Increase in wear rate	Study
Stop-dwell-start	28	0.19	4.75	Roter et al. (2002)
Jogging	40		1.67	Bowsher et al. (2006b)
	40		1.84	Bowsher et al. (2006b)
Lateralisation	28	1.2	6.00	Williams et al. (2004)
	28	1.57	1.57	Williams et al. (2007)
	28	4.62	4.67	Al-Hajjar et al. (2013b)
	36	5.47	15.63	Al-Hajjar et al. (2013b)
	36	1.32	2.2	Williams et al. (2013)
High Angle	28	2.56	2.59	Al-Hajjar et al. (2013b)
	36	0.37	1.06	Al-Hajjar et al. (2013b)
	39	5.25	10.5	Leslie et al. (2009b)
	40	0.69	2.88	Angadji et al. (2009)
	40	1.7	7.08	Angadji et al. (2009)
	52	6.09	64.1	Saikko et al. (2013)
	48	0.33	1.38	Royle (2012)
High Angle + Luxation	48	0.31	1.19	Royle (2012)
High Angle + Lateralisation	28	4.44	4.48	Al-Hajjar et al. (2013b)
	36	4.14	11.83	Al-Hajjar et al. (2013b)
	39	10.5	21.00	Leslie et al. (2009b)

Increasing the inclination angle at which the cup is placed has also shown to influence metal-on-metal wear. Inclination angles can vary due to patient anatomy variations and challenges found during the procedure. Recommended safe zones of 40 ± 10 ° and 15 ± 10 ° for inclination and anteversion respectively have been suggested and widely adopted as guidance (Lewinnek et al., 1978). Clinically the load is applied at an angle of 10 – 15° from the vertical axis (Lancin et al., 2007) yet is applied vertically in simulators, therefore a test conducted at 35° inclination angle, as described in standard testing, correlates to an orientation of 45 – 50 ° as described when implanted.

The increase in the angle moves the area of wear closer to the edge of the cup which can ultimately lead to the head articulating against the rim of the cup as in McKellop's (2007) wear mode. The design and functional arc of the bearings may play an important role in determining the severity of high angle testing. A reduced coverage arc increases the chances of edge loading (De Haan et al., 2008) and therefore, some bearings may experience edge loading at lower inclination angles. Some authors have reported increased steady state wear rates at high inclination angles (Angadji et al., 2009, Leslie et al., 2009b) yet another study at 60° has reported only an increase in run-in wear rates and not steady state wear (Royle, 2012). An increase in wear has also been observed in high angle conditions with 28 mm diameter MoM bearings but not 36 mm diameter (Al-Hajjar et al., 2013b) suggesting that diameter may also influence the severity of high angle conditions.

Lateralisation conditions also produces edge loading conditions, replicating the separation of the femoral head and acetabular cup that may occur during walking (Komistek et al., 2002, Dennis et al., 2001). This has been reported to increase run-in and steady state wear in metal-on-metal bearings to 2.7 mm^3/mc

and 1.75mm^3/mc, respectively, using a 0.8 mm separation. (Williams et al., 2004a). The microseparation occurs during swing phase of the walking cycle (when the load on the joint is low); the lax soft tissues surrounding the hip joint allow the femoral head to separate from the acetabular cup, Figure 2:9A. As stance phase is initiated, and the load on the joint increased, the head connects with the rim of the cup, Figure 2:9B. This is then pushed back into the centre of the cup by the force exerted by the body, Figure 2:9C. This mechanism has been described as Mode 2 wear by McKellop (2007) and proposed as the cause of stripe wear observed in ceramic-on-ceramic implants (Nevelos et al., 2000).

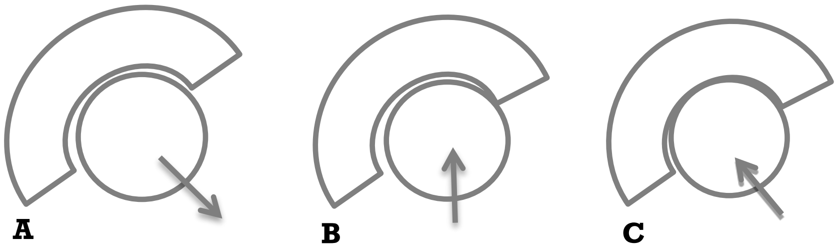


Figure 2:9: Schematic of the microseparation mechanism as it occurs *in vivo*. During swing phase the head separates from the cup (a) and then hits the rim of the cup when the load is reapplied on the joint at heel strike (b) resulting in the head being pushed back into the centre of the cup for stance phase (c)

A wear stripe on metal heads under simulated lateralisation conditions has been observed, measuring 2 mm long and 40 μm deep (Williams et al., 2004a). The introduction of lateralisation at a 45° cup angle has reported a fivefold increase in steady state wear over standard conditions compared to a tenfold increase when the cup angle was increased to 55° (Williams et al., 2008). However, when compared to high angle wear rates, the influence of high angle and lateralisation conditions combined does not appear as significant (Leslie et al., 2009b). Al-Hajjar et al., (2013b) also reported that the angle at which lateralisation occurs does not significantly alter the wear rate whether in 28 mm or 36 mm diameter bearings.

Damage conditions have also been generated in metal-on-metal bearings. Components intentionally damaged by dragging, or luxating, the head from the cup 50 times under a load of 2,500 N after 2 mc of testing at a high angle, and tested for another 2 mc, showed an increased running-in wear rate of 7.37 ± 0.58 mm^3/mc but a steady state wear rate of 0.31 ± 0.02 mm^3/mc, comparable to standard steady state wear (Royle, 2012). This pattern was attributed to the "self-polishing" mechanism observed in metal-on-metal bearings. Heads replaced or rotated after 5 mc also showed a secondary running-in period and then resumed to steady state conditions while heads which had been scratched at a load of 12 N after 5 mc of standard testing showed both increased run-in and steady state wear rate in wrought and cast heads (Hardaker et al., 2011). It has been suggested that the scratched heads may have exhibited a longer running-in period and therefore, steady state wear had not been fully initiated resulting in the higher wear rate. The use of third body abrasives in the form of CoCrMo and titanium particles added at a concentration of 0.0125 mg/mL have shown increases in wear to 4.1 and 6.4 mm^3/mc, respectively (Halim et al., 2014) suggesting abrasive conditions may be highly adverse in this material combination.

2.3.4 Ion Release and Hypersensitivity Reactions

Early failures of current MoM have been observed and attributed to hypersensitivity reactions (Cobb and Schmalzreid, 2006). Pandit et al., (2008) were the first to report the phenomenon of pseudotumours with the majority of cases in female patients who underwent metal-on-metal total hip replacement. Although concern over pseudotumours has primarily focussed on metal-on-metal, there are also reports of pseudotumours in metal-on-polyethylene cases (Bourghli et al., 2010, Walsh et al., 2012).

It is currently believed that these hypersensitivity reactions are the result of the body's reaction to corrosion products (Willert et al., 2005). In CoCrMo bearings, the corrosion products predominately produced are from the alloy namely cobalt and chromium ions (Yan et al., 2006a). Corrosion can be generated from the bearing surfaces as well as the wear particles produced. These particles have been shown to be smaller than those from metal-on-polyethylene bearings, typically on the nanometre scale (Catelas et al., 2003) and therefore 13 to 500 times more metal particle may be produced (Ingham and Fisher, 2000).

These corrosion products can disseminate throughout the body increasing cobalt and chromium measured in the blood; whole and serum, and urine (Brodner et al., 1997, Jacobs et al., 2003, Willert et al., 2005) of patients receiving metal-on-metal bearings, Table 2:12. While the majority of patients possess cobalt and chromium blood levels below 10 ppb, incidences of blood ion concentrations as high as 200 ppb have been reported (Emmanuel et al., 2014, Almousa et al., 2013, Hartmann et al., 2012). Currently, the blood serum levels in metal-on-metal patients are monitored and levels above 7 ppb require further investigation to ensure the bearings are performing well with no hypersensitivity reactions (MHRA, 2012). Studies have shown increasing whole blood cobalt concentration with an increased presence of particles in the synovial hip joint

(De Pasquale et al., 2013) and a Spermann correlation of 0.847 and 0.855 has been reported between cobalt concentration in the synovial joint and cobalt measured in the whole blood or serum respectively (Beraudi et al., 2013). In the synovial joint, cobalt levels as high as 14,285 ppb have been reported (range: 1-14,285 ppb) in revised metal-on-metal hips (Davda et al., 2011).

Table 2:12: The range of cobalt and chromium levels reported in metal-on-metal patients

Sample taken	**Median concentration (range), ppb**		**Study**
	Cobalt	**Chromium**	
Whole Blood	2.21 (0.26-5.63)	1.34 (0.60-3.10)	Vendittoli et al (2010)
Whole Blood	2.7 (0.2-145.3)	2.1 (0.6-68.3)	Newton et al (2012)
Whole Blood	4.82 (0-212.88)	3.05 (0-104.95)	Emmanuel et al 2014)
Whole Blood	28 (0-387)	20 (0-179)	Matthies et al (2014)
Blood Serum	0.7 (0.0-79.3)	0.8 (0.3-25.4)	Hallows et al (2011) Large heads
Blood Serum	0.77 (0.47-1.99)	1.29 (0.68-1.78)	Engh et al (2009)
Blood Serum	1.0 (0.3-14.0)	2.1 (0.3-27.1)	Hallows et al (2011) Small heads
Blood Serum	1.1	-	Brodner et al (1997)
Blood Serum	1.11 (0.35-5.24)	1.49 (0.10-7.59)	Johnson et al (2013)
Blood Serum	1.2	1.5	Hallab et al (2012)
Blood Serum	1.3 (0.5-285.3)	1.9 (0.5-151.5)	Hartmann et al (2012)
Blood Serum	1.33 (0.34-5.32)	1.72 (0.21-6.65)	Savarino et al (2002)
Blood Serum	1.9 (0.5-10.8)	2.1 (0.5-14.3)	Kwon et al (2011) No Pseudotumour
Blood Serum	2.3	1.6	Hasegawa et al (2012)
Blood Serum	2.86 (0.30-10.44)	2.94 (0.35-7.62)	Johnson et al (2013)
Blood Serum	9.2 (4.8-22.5)	12.0 (3.8-22.8)	Kwon et al (2011) Pseudotumour
Blood Serum	10.8 (0.3-47.2)	14.5 (0.7-60.6)	Macnair et al (2013)
Blood Serum	54.19 (2.55-195.61)	40.42 (2.07-142.46)	Almousa et al (2013)
Erythrocytes	0.42 (0.27-0.71)	1.1 (0.6-1.70)	Engh et al (2009)
Urine	4.55 (2.07-14.22)	1.92 (1.08-3.74)	Engh et al (2009)
Synovial joint	106.25 (13-769)	179.5 (19-661)	De Smet et al (2008) No Metallosis
Synovial joint	1127 (2-14,285)	1337 (0-190,416)	Davda et al (2011)
Synovial joint	2,185 (110-5,120)	5,136.5 (155-29,080)	De Smet et al (2008) Metallosis

Several *in vitro* studies have considered the cobalt and chromium release in hip simulators showing large amounts of cobalt and chromium, Table 2:13. While these tests are conducted in different volumes and therefore provide different concentrations, all tests suggest that the majority of corrosion occurs during the run-in period with more cobalt released than chromium. The relationship between wear and ionic release has also been investigated reporting linear correlations between wear and cobalt release with R^2 value of 0.94 (Al-Hajjar et al., 2013b) and a Pearson's correlation of 0.99 (Royle, 2012). A weaker relationship between wear and chromium release has also been established with a R^2 vale of 0.65 (Al-Hajjar et al., 2013b) but a Pearson's correlation of 0.99 (Royle, 2012).

Table 2:13: Summary of cobalt and chromium release from MoM bearings under standard hip simulator conditions

Time Period, mc	Diameter, mm	Co Concentration, µg/L	Cr Concentration, µg/L	Study
Run in	36	6,000	2,000	Williams et al., (2007)
0-0.13	39	153,838	63,497	Leslie et al., (2008)
0-0.13	55	185,207	70,672	Leslie et al., (2008)
0-0.2	32	41,000	18,500	Ishida et al., (2009)
0-0.33	28	15,000	9,000	Fisher et al., (2004)
0.8-1.0	32	11,000	4,100	Ishida et al., (2009)
0.13-0.5	39	186,574	68,927	Leslie et al., (2008)
0.13-0.5	55	25,015	7,010	Leslie et al., (2008)
Steady state	36	1,500	500	Williams et al., (2007)
2.5-3.0	32	8,600	3,850	Ishida et al., (2009)
3.3-3.6	39	3,498	1,099	Leslie et al., (2008)
3.3-3.6	55	2,981	801	Leslie et al., (2008)
0-1.66	28	150,000	60,000	Saikko et al., (1998)
0-2	48	9,289	3,435	Royle (2012)
0-2.82	28	90,000	30,000	Saikko et al., (1998)

The increase in metal wear in adverse testing, increases cobalt and chromium levels with 23,170 and 8,191 μg/L reported in components damaged and tested for 2 million cycles (Royle, 2012). Similar increases in cobalt release have been reported in high angle and lateralisation conditions (Al-Hajjar et al., 2013b). Conversely, the addition of bone cement particles in metal-on-metal bearings has shown to inhibit ionic release possibly due to adhesion of the bone cement to the bearings surfaces (Saikko et al., 1998). In this test, bone cement particles were added a at a concentration of 0.1 mg/mL which was probably too low to induce an increase in wear and consequent increase in ion release.

2.3.5 Ceramic coatings

Ceramic-on-ceramic bearings have reported lower wear rates and ionic release than metal-on-metal bearings under standard and adverse simulator conditions (Williams et al., 2007). However, fracture of these bearings has been reported under lateralised conditions (Stewart et al., 2003) and the diameter available is limited to 48 mm (Rodriguez and Cooper, 2013). Ceramic surface coatings of metal-on-metal bearings, an alternative, have also been shown to reduce wear and ionic release in standard simulator studies (Gispert et al., 2007). These coatings can be applied to one or both bearing surfaces with various coating methods utilised, Table 2:14.

Table 2:14: Wear rates and ionic release in standard hip simulator test conditions for hard-on-hard coated bearings

Bearing couple	Coating Method	Wear rate, mm^3/mc		Concentration, µg/L (Time Period)		Study
		Run in	Steady State	Co	Cr	
TiN-CoCrMo	AEPVD	2.4 ± 0.25	0.2 ± 0.01	10,000 (0-0.33 mc)	50,000 (0-0.33 mc)	Fisher et al. (2002)
CrN –CoCrMo	AEPVD	0.17 ± 0.1	0.1 ± 0.08	800 (0-0.33 mc)	1,000 (0-0.33 mc)	Fisher et al. (2002)
CrN –CoCrMo	PAPVD	-	2.4	-	-	Ortega-Saenz et al. (2013)
CrCN-CoCrMo	AEPVD	0.12 ± 0.17	0.1 ± 0.1	500 (0-0.33 mc)	300 (0-0.33 mc)	Fisher et al. (2002)
DLC – CoCrMo	PACVD	0.08 ± 0.02	0.03 ± 0.02	800 (0-0.33 mc)	800 (0-0.33 mc)	Fisher et al. (2002)
DLC – CoCrMo	BALINIT	-	1.3	-	-	Ortega-Saenz et al. (2013)
TiN/CrN-CoCrMo	PAPVD	-	27	-	-	Ortega-Saenz et al. (2013)
DLC-DLC	PPAD	-	<0.0001	-	-	Lappalainen et al. (2003)
CrN-CrN	AEPVD	0.15	0.1	-	-	Williams et al. (2004a)
CrN-CrN	AEPVD	0.1	0.00003	900 (0-0.33 mc)	300 (0-0.33 mc)	Fisher et al. (2004)
CrN-CrN	AEPVD	0.2 ± 0.05	0.03 ± 0.03	599 0-0.5 mc) 244 (3.3-3.6 mc)	7,424 (0-0.5 mc) 585 (3.3-3.6mc)	Leslie et al. (2009a)
CrN-CrN	EBPVD	1.12 ± 0.37	0.00 ± 0.00	4 (0-2.00 mc)	2,465 (0-2.00 mc)	Royle (2012)
CrN-CrN	AEPVD	0.3 ± 0.1	0.02 ± 0.05	427 (0-0.5 mc) 120 (3.3-3.6 mc)	4618 (0-0.5 mc) 487 (3.3-3.6 mc)	Leslie et al. (2009a)
CrCN-CrCN	AEPVD	0.09	0.04	600 (0-0.33 mc)	400 (0-0.33 mc)	Fisher et al. (2004)
Ag-CrN – Ag-CrN (17wt.%)	EBPVD	0.74 ± 0.22	0.05 ± 0.09	8 (0-2.00 mc)	1,060 (0-2.00 mc)	Royle (2012)
Ag-CrN – Ag-CrN (41wt.%)	EBPVD	0.67 ± 0.19	0.11 ± 0.10	32 (0-2.00 mc)	812 (0-2.00 mc)	Royle (2012)
CrN-DLC	AEPVD/ PACVD	0.06	0.03	200 (0-0.33 mc)	400 (0-0.33 mc)	Fisher et al. (2004)
CrN-TiN	AEPVD	0.03	0.06	40 (0-0.33 mc)	300 (0-0.33 mc)	Fisher et al. (2004)
TiN-TiN	AEPVD	0.08	0.1	30 (0-0.33 mc)	200 (0-0.33 mc)	Fisher et al. (2004)

Reduced wear rates have been reported in arc evaporative PVD chromium nitride (CrN) and chromium carbonitride (CrCN) coated heads, as well as plasma assisted CVD diamond-like carbon coated heads against uncoated CoCrMo cups (Fisher et al., 2002). Further wear reduction has been observed when coating both bearing surfaces (Lappalainen et al., 2003, Fisher et al., 2004) and has seen a tenfold reduction in ion release for both cobalt and chromium, even with chromium rich coatings.

However, not all coatings are successful at reducing wear under standard conditions. Titanium nitride (TiN)-on-metal have increased wear rates due to presence of microdroplets from coating despite polishing the surface which resulted in abrasive wear of the uncoated cup; also increasing cobalt and chromium ion levels as well. TiN-on-TiN and CrCN-on-CrCN coatings have shown cohesive failure of bearings. DLC-on-CrN coatings have shown areas of cracking on the DLC cup surface and isolated failure has been observed in CrN-on-CrN bearings.

CrN coatings have been the most successful, producing lower wear than other coatings. These coatings are achieved using physical vapour deposition methods (PVD) in which coatings are produced from a metal solid form as opposed to gaseous forms in methods such as chemical vapour deposition (CVD), in a high vacuum environment (Astakhov, 2006). The evaporated or sputtered metal then reacts with a gaseous state (such as nitrogen) at relatively low pressures of 10^{-3} to 10^{-2} torr (Davis, 1995). This method offers several advantages over CVD including lower deposition temperature, no thermal cracks within the coating and a reduction in residual stresses (Astakhov, 2006, Davis 1995, Stephenson and Agapiou, 2005). Two methods of producing PVD CrN coating have been utilised in the field reporting promising results; namely arc evaporative PVD (AEPVD) and electron beam PVD (EBPVD) coatings (Qin, 2010). These techniques differ by the method in which the coating material is vaporized. AEPVD uses a high current arc and EBPVD uses an electron beam in a vacuum environment (Mattox, 2010). While AEPVD is a more commonly reported to be used method than EBPVD, this process tends to produce a rougher surface finish than EBPVD coatings due to the presence of large microdroplets formed by the cathode during the growth process (Fuentes et al., 2005).

In long term testing at diameters of 39 mm and 55 mm diameters, AEPVD coated CrN-on-CrN bearings have produced significantly (88 and 71% respectively) less wear than uncoated MoM and released less cobalt and chromium ions after 3.6 mc of standard testing (Leslie et al., 2009a). A similar wear reduction of 67% was reported in EBPVD CrN coated 48 mm diameter bearings and the amount of cobalt released was also significantly reduced (Royle, 2012). Under standard wear conditions, the AEPVD CrN coatings have been reported to produce lower run-in wear rates than the EBPVD CrN coatings as the AEPVD coatings were polished before testing and therefore the increased run-in wear of the EBPVD is attributed to the removal of microdroplets formed during coating. Both coatings produce low, near negligible steady state wear rates (Fisher et al., 2004, Royle, 2012). Nitriding the cobalt surface and then coating with CrN (Duplex), however, has produced large amounts of wear and high levels of cobalt attributed to the change in surface chemistry observed during the nitriding process (Royle, 2012).

Adverse tests have been performed in CrN-on-CrN bearings including high angle, luxation damage and lateralisation, Table 2:15. In 28 mm diameter CrN bearings coated via AEPVD, lateralisation at a distance of 0.8 mm has generated superficial damage in the coating due to the high stresses occurring during heel strike which increased the steady state wear (Williams et al., 2004a). Similar failures have been observed in larger (39 mm diameter) CrN coated bearings under lateralisation conditions leading to wear rates as high as 54.91 mm^3/mc (Leslie et al., 2013). In bearings coated via electron beam PVD (EBPVD), high angle tests have been shown to increase wear and ionic release (Royle, 2012). Heads damaged under luxation conditions and run for a further 2 million cycles at high angle conditions also showed increased wear and cobalt release, suggesting the coating on the cup had worn through.

To enhance lubrication of the EBPVD CrN coated bearings, silver has been added at different quantities and tested under similar conditions to CrN-on-CrN (Royle, 2012). Under standard conditions, increasing the content of silver (Ag) from 17 wt% to 41 wt% appeared to decrease initial running in wear and chromium release, although all wear and ionic release was lower than the uncoated MoM bearings. Under high angle conditions, this trend was maintained and when luxation damage and 2 million cycles of further testing were conducted the lower silver concentration coatings failed, producing large amounts of wear and cobalt. High (51wt%) CrN-Ag coated metal-on-metal bearings maintained a lower wear rate and ionic release than the uncoated bearings under the same conditions. While this suggests a potential for these bearings to reduce wear and minimise the risk of hypersensitivity reaction, it should be noted that the Ag/Cr ratio decreased over 4 million cycles of testing highlighting a need for longer term testing.

Table 2:15: Summary of wear rate in adverse metal-on-metal hip simulator tests where at least one metal bearing surface has been coated

Bearing couple	Coating Method	Diameter, mm	Test conditions	Wear rate, mm^3/mc		Study
				Run in	Steady State	
CrN-CrN	AEPVD	28	Low Swing phase load	0.05	0.02	Williams et al. (2004a)
CrN-CrN	AEPVD	28	Lateralisation	0.05	0.55	Williams et al. (2004a)
CrN-CrN	AEPVD	39	Lateralisation	1.80 ± 3.13	18.04 ± 27.65	Leslie et al. (2013)
CrN-CrN	EBPVD	48	High Angle	1.11 ± 0.24	0.11 ± 0.14	Royle (2012)
CrN-CrN	EBPVD	48	Head Damage	2.57 ± 1.31	1.41 ± 0.04	Royle (2012)
Ag-CrN – Ag-CrN (17wt.%)	EBPVD	48	High Angle	1.95 ± 0.85	0.05 ± 0.02	Royle (2012)
Ag-CrN – Ag-CrN (17wt.%)	EBPVD	48	Head Damage	18.62 ± 12.82	60.17 ± 41.59	Royle (2012)
Ag-CrN – Ag-CrN (41wt.%)	EBPVD	48	High Angle	1.01 ±0.45	0.16 ± 0.04	Royle (2012)
Ag-CrN – Ag-CrN (51wt.%)	EBPVD	48	High Angle	0.78 ± 0.21	0.17 ± 0.04	Royle (2012)
Ag-CrN – Ag-CrN (51wt.%)	EBPVD	48	Head Damage	2.14 ± 0.88	0.26 ± 0.02	Royle (2012)

2.4 Aims and Objectives

Adverse tests depend on the component design and material combination. Metal-on-metal components have been shown to be sensitive to edge loading and metal-on-polyethylene are susceptible to abrasive conditions. Metal-on-metal bearings have raised greater concerns over metal corrosion products in the body with elevated blood cobalt levels reported for these bearings, however more recently high levels have also been reported for metal-on-polyethylene bearings. The latest generation of vitamin-E doped polyethylene has been optimised to reduce polyethylene wear but both this surface and the metal bearing surface may be susceptible to roughening and roughened conditions. The adoption of a scratch resistant ceramic coating may provide wear reduction under standard and challenging hip simulator conditions possibly reducing cobalt release as well. Silver containing coatings may provide a further benefit as silver has the potential to act as an anti-bacterial agent. However, adverse testing particularly lateralisation is required to test the adhesion of the coating as this is vital to the success of the bearing.

The aim of this thesis is to establish the potential of novel ceramic coatings on the metal bearing surfaces of metal-on-polyethylene and metal-on-metal bearings to reduce both wear and ionic products and thereby create a device suitable for implantation in patients. This will be conducted through the adoption of appropriate adverse testing methods which challenge the adhesion of the coating. Throughout testing, gravimetric wear, cobalt release and particle analysis methods will also be utilised to provide an understanding of the wear mechanisms occurring.

3 Methods Development

3.1 Wear testing

All wear testing was conducted on an eight station orbital hip simulator (MTS Systems, USA). Hip components were mounted in an anatomical position with cups mounted at 35 degrees to the horizontal on self-aligning bearings, and the heads moving relative to the cups due to a sun and planetary gear system. The heads were mounted on tapers on cams which produced consistent 23 degrees of biaxial rocking, Figure 3:1. Loading was applied through a servo hydraulic system controlled by MTS FlexTest 40 software, triggered with each rotation. The load was tuned for each material combination to ensure consistency between tests.

Figure 3:1: Photograph showing stations of the hip simulator during testing

All heads were mounted on fixtures coated with PTFE except over the taper to prevent metal ion contamination from these fixtures, Figure 3:2. The base of these fixtures screwed into clear acetal chambers which held 600 mL of serum lubricant. Three pins at the bottom of the chambers connected to the hip simulator cams.

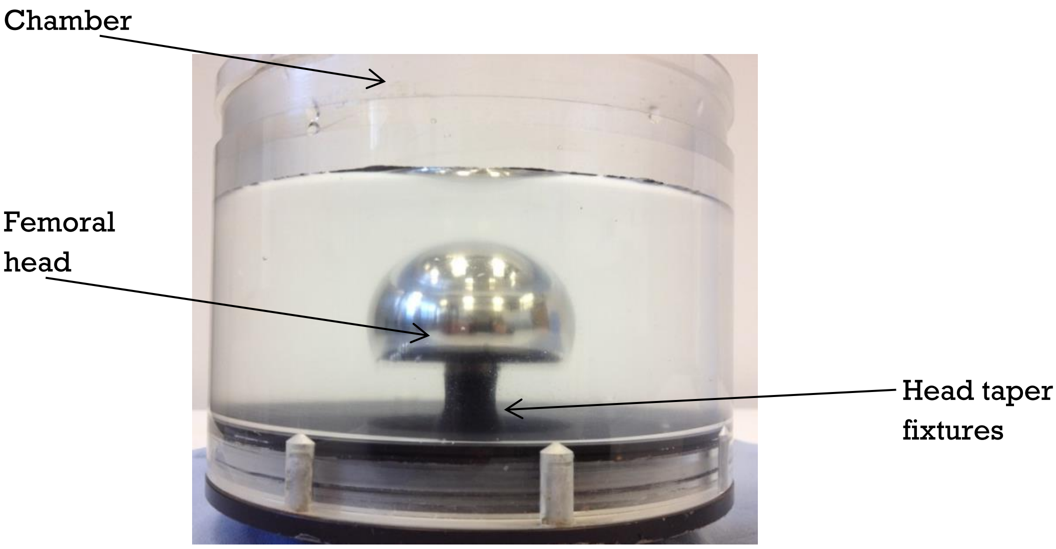


Figure 3:2: Photograph of head fixturing with head mounted

Metal cups were custom manufactured to include a cylindrical peg at the back of the cup. This peg allowed for mounting by inserting into the cup holders and was subsequently clamped in place to prevent rotation. The fixtures were coated with PTFE and a latex balloon was placed over the outside of the cup fixture and the back of the cup, Figure 3:3, allowing only metal ions from the bearing surface of the cup to be released into the test lubricant.

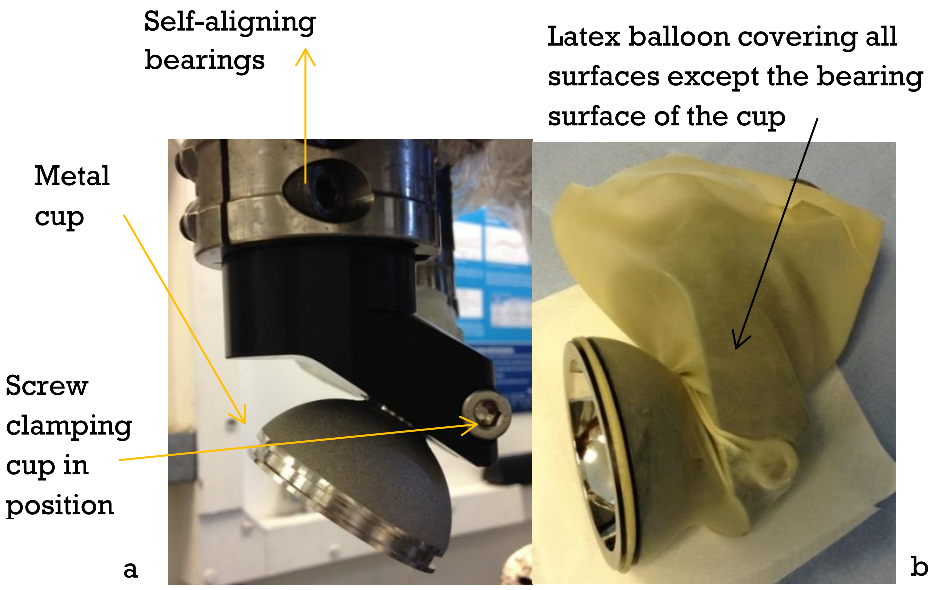


Figure 3:3: Metal cup fixturing assembly (a) in hip simulator without latex balloon covering and (b) covered by latex balloon

Polyethylene liners were placed in CoCrMo metal shells and inserted into acetal holders in stainless steel fixturing, Figure 3:4b. These fixtures were not coated in PTFE but the soak controls were held in similar fixtures; any ion release from the fixtures could be measured. To prevent rotation of the liners, metal plates with three protrusions where manufactured to fit into three corresponding slots cut into the liners, Figure 3:4a. The plates were screwed onto the face of the stainless steel fixtures, completing the assembly of the polyethylene liner in the fixtures, Figure 3:4c.

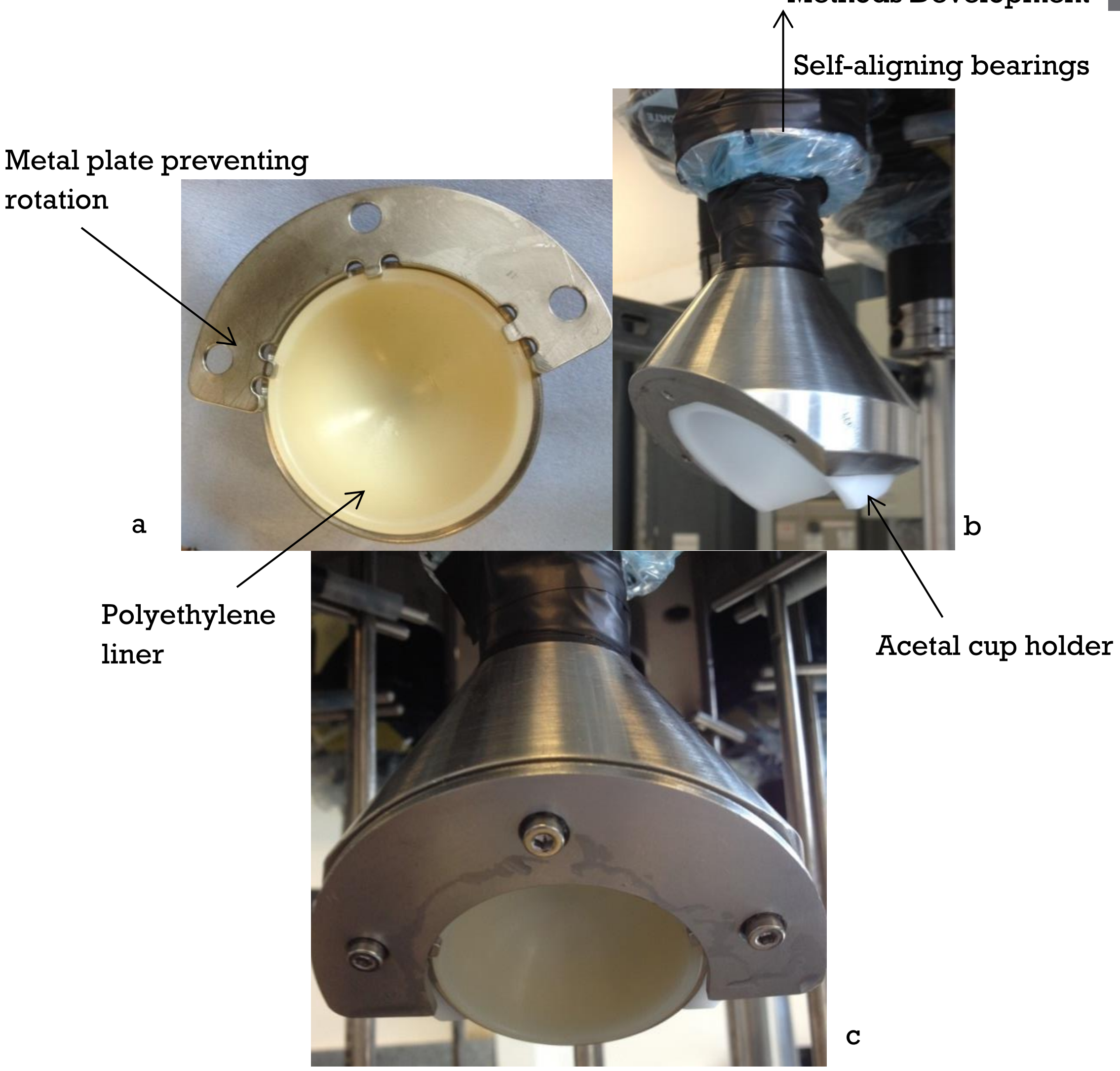


Figure 3:4: Fixturing used for polyethylene cups showing (a) the liner and shells with a plate to prevent rotation, (b) the fixturing itself and (c) the complete set-up

Wear was determined gravimetrically using balances (Precisa 404a and 92SM-202a, UK). Before wear measurement, the components were cleaned. Metal-on-polyethylene bearings were cleaned based on ISO 14242-2 (2000) featuring 10 minute intervals in an ultrasonic bath in deionised water and detergents before drying with inert gas and propan-2-ol and were left to dry for 12 hours before mass measurements were taken, Appendix A. The metal-on-metal bearings were cleaned following the same protocol but the duration of each step was doubled (Royle, 2012).

During wear assessment of the metal components, a metal head and cup were used as mass controls and five measurements of each test component relative to the mass were recorded, with additional measurements taken if these values deviated by more than 0.2 mg. Wear was calculated as mass loss and converted to volume using the density of a cobalt chrome alloy, chromium nitride and silver doped chromium nitride; 8300, 5900 and 9000 kg/m^3 respectively.

The mass loss of the polyethylene liners was determined using the same conditions as the metal components with the addition of an anti-static wristband worn during the weighing process. Soak controls, not tested under load but placed in 25 % dilute bovine serum beside the test components and therefore subjected to similar environmental conditions as the test components, were also weighed at each gravimetric interval. The mean mass gain in the soak controls due to fluid absorption was added to the mean mass loss of each test component to provide the wear mass loss. Wear mass loss was converted to volume loss using a density of 942 kg/m^3. The data produced in this thesis was analysed by performing a Student's t-test to determine significance ($p<0.05$ unless otherwise stated).

Newborn calf serum was used as a lubricant, diluted to 25% with deionised water. Sodium azide was added at a concentration of 1% (wt/vol) to retard bacterial growth. The lubricant was replaced every half a million cycles or gravimetric interval, whichever occurred first. Test fluid was stored at -20 °C for particle and ion analysis to reduce decomposition of particles as observed in Figure 3:5.

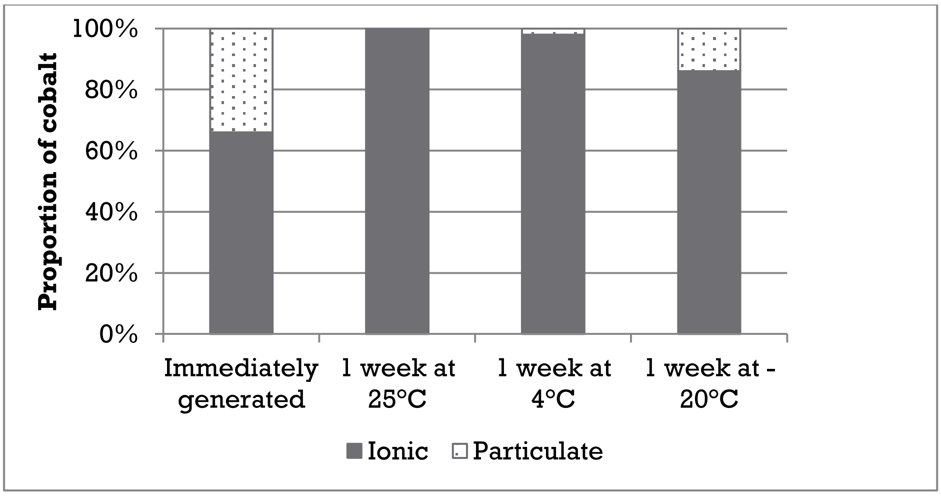


Figure 3:5: Increasing proportion of ionic cobalt in 100% bovine serum after 1 week of storage at different temperatures

Degradation during storage at -20°C was observed with time and therefore cobalt analysis was performed as soon after testing as reasonably possible, within one month. Increasing levels of ionic cobalt concentration of CoCrMo nanoparticles stored in 100% bovine serum, however, was reported following 7, 14, 28 and 56 days of storage, Figure 3:6. This corrosion process occurred rapidly during the first 14 days, increasing from 64% to 82%, however following this, the rate of degradation slowed turning completely ionic after 56 days. As the particles were stored in 100% bovine serum, the corrosion process observed may have occurred at a faster rate than would occur in 25% diluted bovine serum, as increased corrosion has previously been reported in bovine serum compared to saline suggesting that the proteins present may accelerate the dissolution process (Yan et al., 2009).

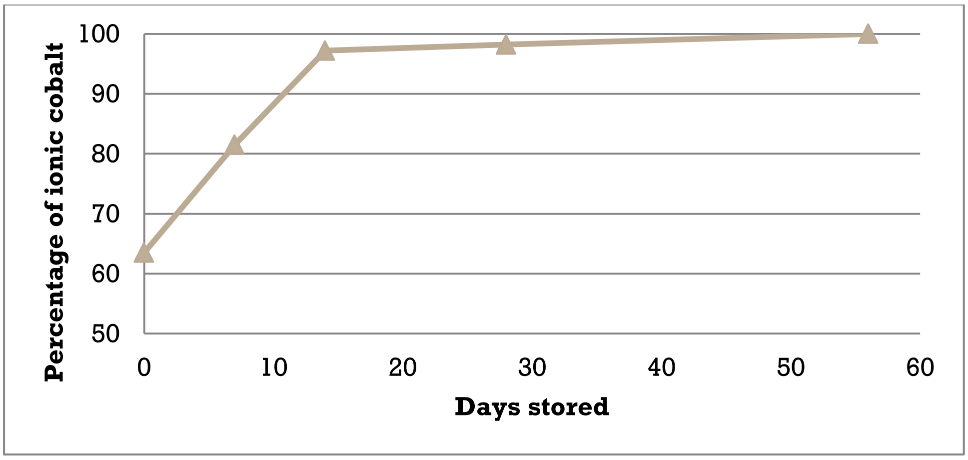


Figure 3:6: Degradation of cobalt into an ionic form over time during storage at -20°C

3.1.1 Standard test conditions

Under standard conditions the load profile was produced according to ISO 14242-3 (2009) at a frequency of 1 Hz with a double peak load of 3,000 N and swing phase load of 300 N as shown in Figure 3:7. The load followed the walking gait cycle starting in heel strike when the foot would initially contact the ground and the load is high. The load remains high, replicating as the leg takes the weight of the body (stance phase) until toe-off and the removal of load from the leg (swing phase) (Scott, 1963). Every cycle correlated to one step of the right hip with 23° of flexion/extension and abduction/adduction. This is less flexion than would be experienced in the hip (approximately 37°) while more adduction, abduction and extension are created on the hip simulator than would be experienced *in vivo* (Besier et al., 2003).

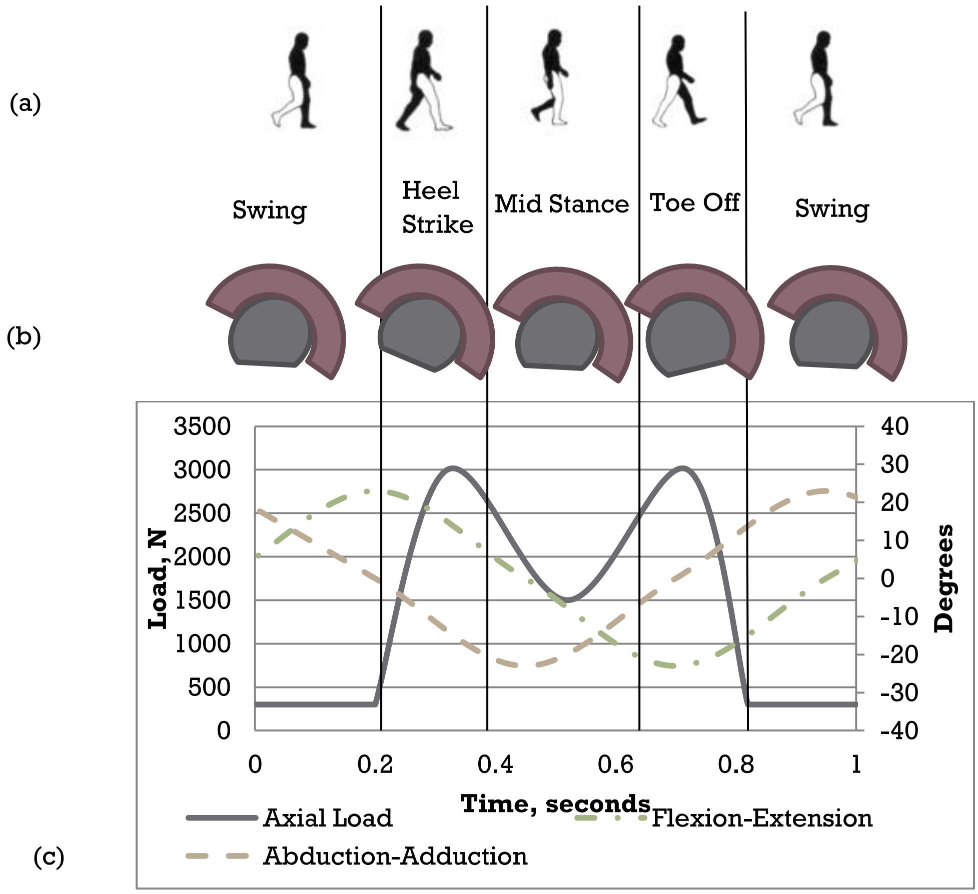


Figure 3:7: One cycle corresponding to one step of walking showing (a) the phases of the gait cycle, (b) the position of the hip and (c) the inputted load, flexion/extension and abduction/adduction experienced on the hip simulator. Walking images taken from Chan and Rudins (1994)

3.1.2 Third body test conditions

Bone cement and alumina particles were added to the test fluid to produce third body conditions in metal-on-polyethylene tests. These utilised the same kinetic and kinematic conditions as standard test conditions with only changes made to the lubricant. In test conditions, third body particles were weighed and added directly to each station to ensure the same concentration was achieved. The continuous motion of the hip simulator kept the particles in suspension throughout the test duration.

Bone cement particles were created from pre-polymerised bone cement powder (Stryker Howmedica, USA.). A particle size analyser (Mastersizer, Malvern Instruments, UK) was used to characterise the particle distribution showing a bimodal distribution with modes of 1.8 and 24.6 µm (range 0.3 -138.0 µm). The bimodal distribution represents different components in the bone cement mixture. The larger particles between 4 and 140 µm (mode: 24.606 µm) are spherical methyl methacrylate stryrene comprising of 75% of the total powder, Figure 3:8b, whilst the smaller flakes below 4 µm (mode: 1.7825 µm) represent polymethylemethacrylate (15%) and barium sulphate (10%), Figure 3:8a. The powder was added at a concentration of 5 mg/mL as described by Wang and Essner (2001) to each station at the start of testing and after each gravimetric interval, when fresh serum was added to the chambers.

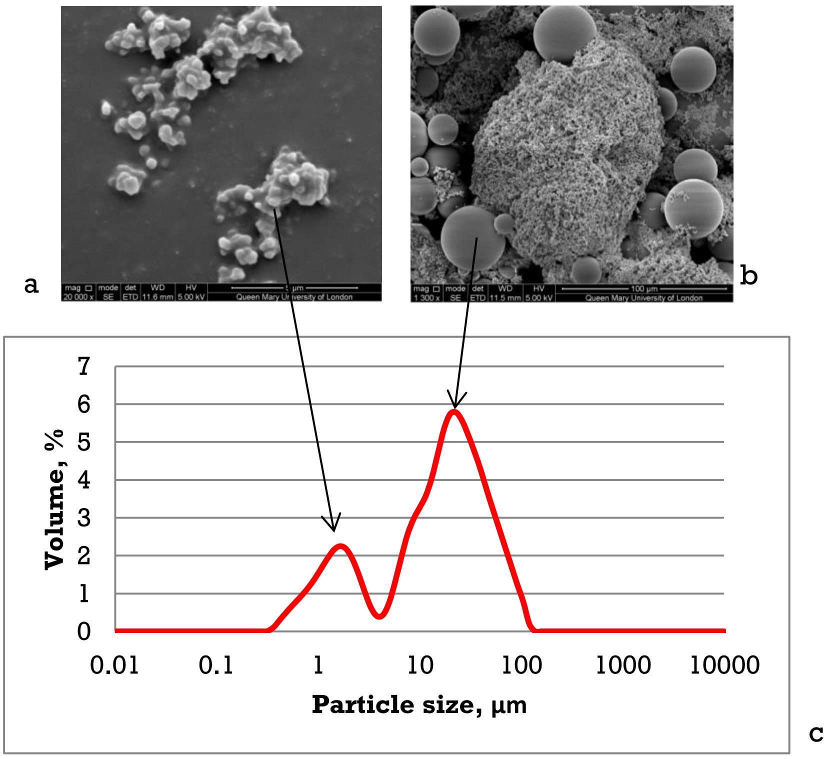
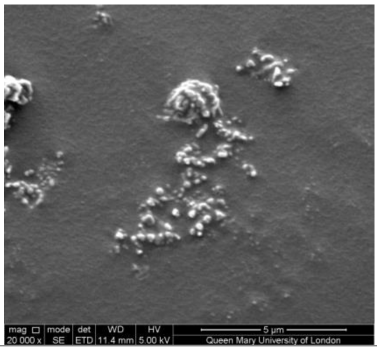


Figure 3:8: Scanning electron microscope images of (a) small polymethylmethacrylate and barium sulphate particles, (b) these particles interspersed with larger methylmethacrylate styrene particles and (c) their resultant particle distribution

Alumina powder was used as a more severe third body condition at a concentration of 0.15 mg/mL in the test fluid as described by Bragdon et al. (2004). The alumina particles were manufactured (Buehler Micropolish, USA) and characterised using a particle size analyser (Mastersizer, Malvern Instruments, UK). These particles were smaller than the total bone cement particles, less than 10 μm, and showed a bimodal distribution with modes of 0.8 and 3.1 μm, ranging from 0.6 – 5.3 μm, Figure 3:9. These particles were similar in range to those of the smaller polymethylmethacrylate and barium sulphate particles.



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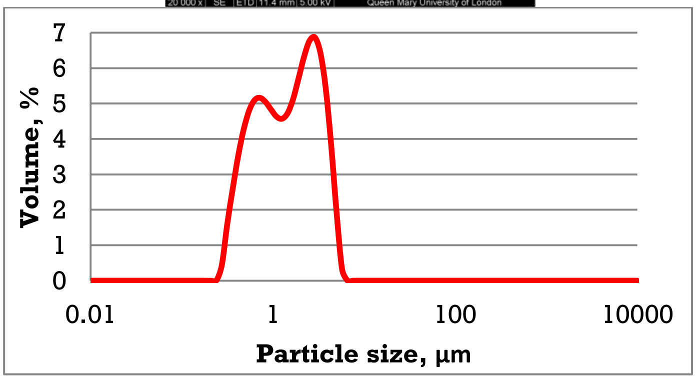


b

Figure 3:9: Characterisation of alumina particles (a) scanning electron microscope image and (b) resultant particle distribution

3.1.3 Jogging test conditions

The gait cycle during walking and jogging is different which alters the loading and kinematics of the hip joint. In the *in vitro* walking cycle, as shown in Figure 3:7, the stance phase of each foot is 60% of the total cycle and so periods of double stance, where both feet are on the ground, occur *in vivo* (DeLisa, 1998). As jogging is initiated, the duration of stance phase decreases to 36-39% of the gait cycle, preventing both legs from touching the ground at the same time and instead resulting in "double float" when both feet are in the air (Novachek, 1998). Bergmann et al (1993) described the change in loading with jogging in patients who had received a total hip replacement with a reduced heel strike and a single peak load of 4,500 N. It has been reported that heel strike in jogging can vary and is highly dependent on the individual's running style with some possessing large heel strikes and others exhibiting no heel strike (Schmitz et al., 2014). The rate of this loading is also highly dependent on running style (Schmitz et al., 2014). Changes in heel strike have also shown to alter the peak force produced by ±10% as well as the moments recorded in the hip (Bergmann et al., 1995).

The simulated jogging in the current study included a small heel strike to initiate loading and completed by toe off period. This load profile was based on that described by Bowsher and Shelton (2001) and lasted 0.55 seconds, Figure 3:10. This was conducted at three different speeds of 1, 1.5 and 1.75 Hz (slow, medium and fast) lasting 14, 400 cycles each. In order to keep as many variables constant as possible, the same 0.55 second load profile was utilised at all three speeds, resulting in a reduced swing phase with increasing speed. Due to the increased speed accompanied in medium and fast jogging conditions, the chambers containing the test fluid were sealed to prevent spillage. Although in the body, flexion, extension, abduction and adduction increase during jogging in an attempt to stabilise the upper body (Novachek, 1998), these could not be altered in the hip simulator and so remained identical to that under standard walking conditions .

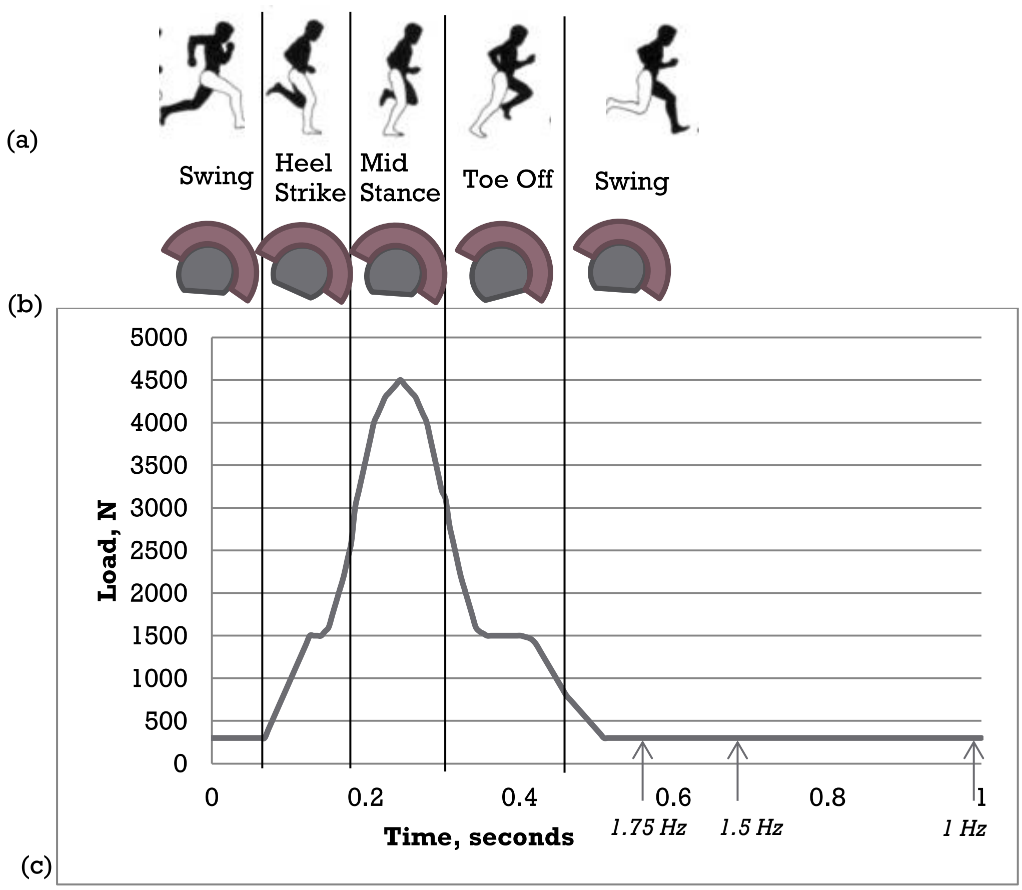


Figure 3:10: One cycle of jogging showing the relationships between (a) the jogging gait cycle, (b) the head and cup position and (c) the inputted load profile used in jogging tests. Jogging images from Chan and Rudins (1994)

3.1.4 Removed Swing Phase Load conditions

The swing phase load was reduced from 300 N in the standard walking cycle to 0 N which resulted in a separation between the head and the cup. The load profile maintained a double peaked profile which a smaller heel strike peak of 1,500 N and a larger peak load of 2,500 N, as described in other simulator studies (Royle, 2012), Figure 3:11.

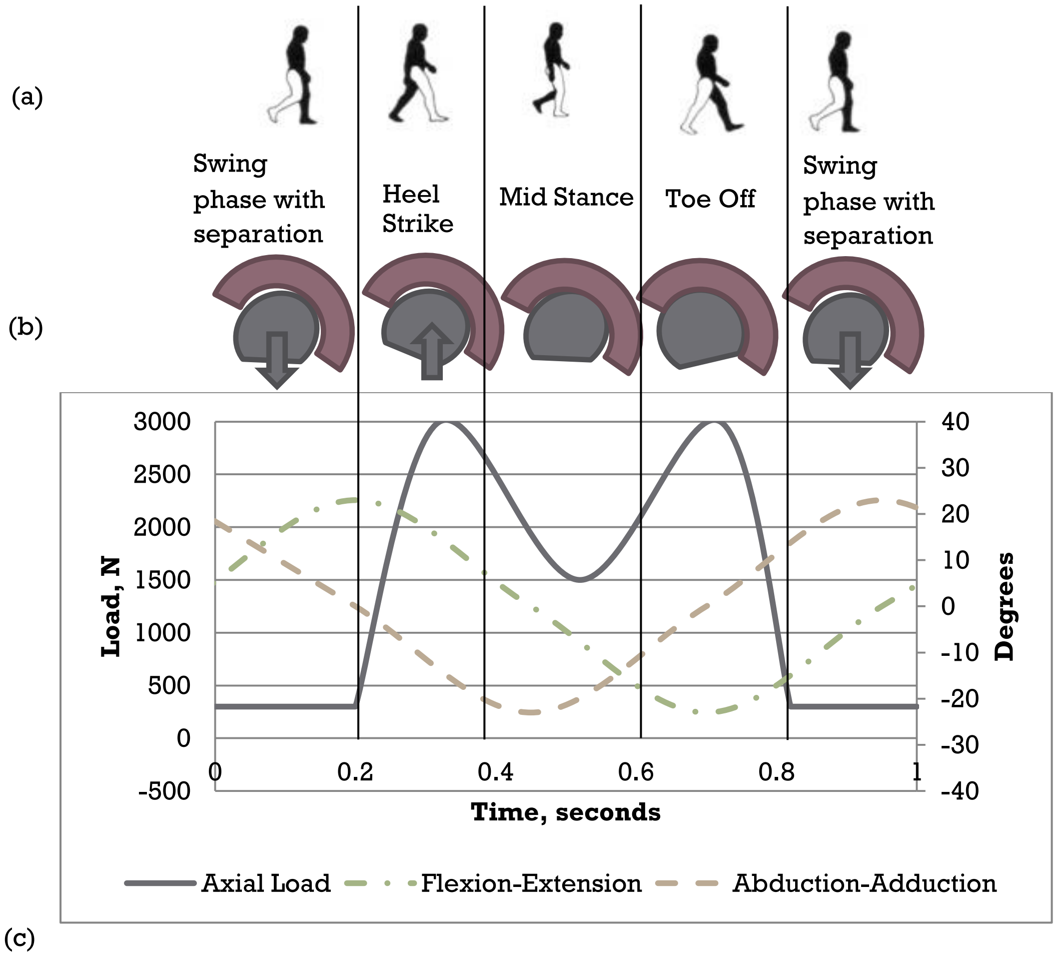


Figure 3:11: One cycle with the swing phase load removed showing (a) the gait cycle phases during walking, (b) the position of the head and cup and relative movement from each other and (c) the input load, flexion/extension and abduction/adduction. Walking images taken from Chan and Rudins (1994).

Aluminium blocks were placed under each station to limit the vertical separation to 1 mm, Figure 3:12. The aim of these blocks was to provide consistent separation between cycles of each station when the swing phase load was removed.

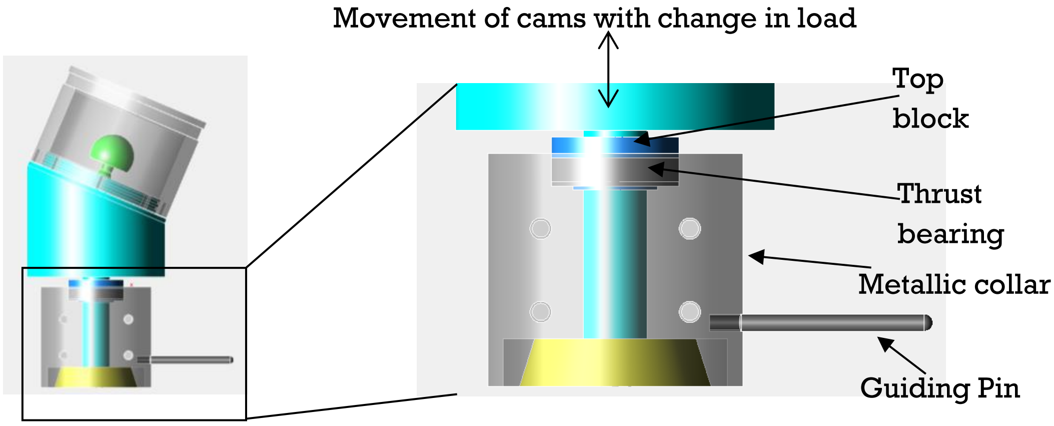


Figure 3:12: CAD model showing the elements of the aluminium blocks designed to restrict vertical movement of the head during the removal of swing phase load

As the load was removed during swing phase, the cams on which the heads were mounted lowered. The cams contacted a metallic collar placed underneath which took the load of the cams, head and fixturing. As the cams rotated throughout the load cycle, a thrust bearing and top block were placed around the piston of these cams and rotated with cams to minimise friction between the cams and metallic collars.

The vertical movement measured using the linear differential transformers (LDT) in the hip simulator showed that the blocks limited the vertical separation following the removal of swing phase load. However, the mean vertical movement produced was 1.04 ± 0.05 mm, Figure 3:13, which was higher than the 1 mm set suggesting that the design was under tolerance, yet consistent.

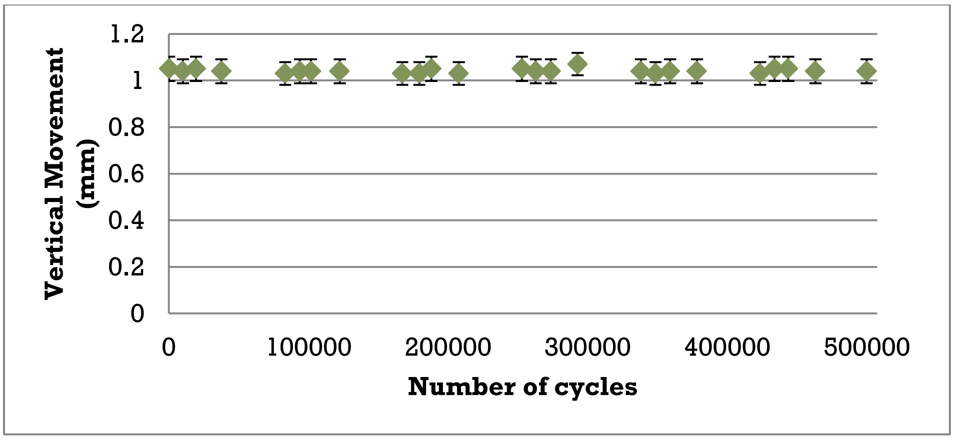


Figure 3:13: Mean vertical movement during swing phase in the presence of the aluminium blocks over 500000 cycles (± 1 sd)

3.1.5 Lateralisation test conditions

In order to produce rim contact between the head and cup, the cup was moved medially during swing phase to represent lateral movement of the head. To achieve this separation during swing phase, the load profile as described in section 3.1.4 was applied enabling separation of the head and cup and therefore displacing the cup with greater ease. The head would then contact the rim of the cup with the increased load forcing the cup back into its original position, Figure 3:14.

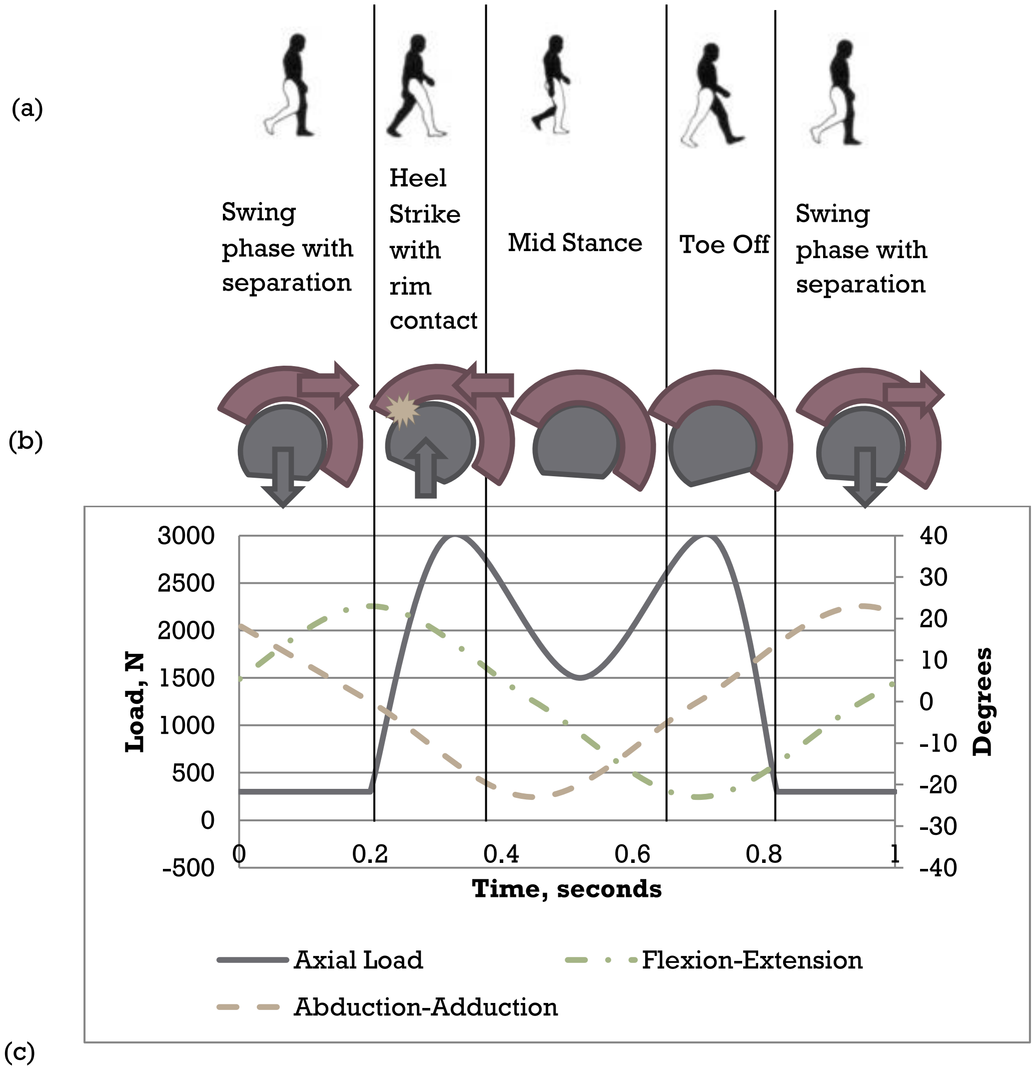


Figure 3:14: One lateralisation cycle showing (a) the gait cycle phases during walking, (b) the position of the head and cup and relative movement from each other and (c) the input load, flexion/extension and abduction/adduction. Walking images taken from Chan and Rudins (1994).

A spring force of 2.37 N was observed to generate a displacement of the cup and not interfere with the self-aligning movement of the cup during stance phase of loading and was therefore utilised. When the load was applied, the spring force did not displace the cup medially and the head and cup articulated against each other as observed during standard walking conditions, Figure 3:15a. However, as the load was removed (during swing phase), the spring force applied from the outside of the hip simulator displaced the cup, Figure 3:15b. An aluminium stopper was designed into the spring mechanism to restrict this medial movement of the cup to 0.7 mm.

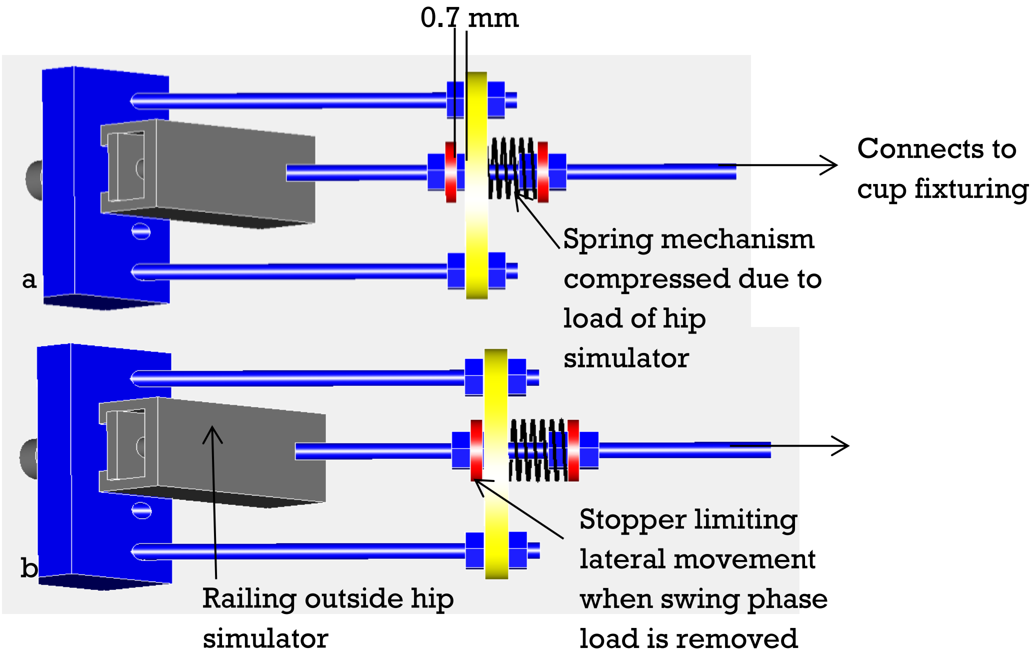


Figure 3:15: Annotated CAD drawing of the spring mechanism used to (a) allow the head to articulate against the centre of the cup when loading is applied and (b) provide 0.7 mm lateral displacement of the cup when the load is removed

Due to the self-aligning nature of the cup fixturing, movement of these cup fixtures was observed during standard walking conditions and found to produce a small (0.1 mm) amount of movement. This lateral/medial movement was measured using a dial gauge indicator under different swing phase loads, Figure 3:16, showing increased displacement of the cup with reduced swing phase load. At 0 N swing phase, when the components wereseparated, the movement increased to 0.3 mm which may suggest that the cup was repositioned during this separation. However, the introduction of the lateralisation mechanism increased the amount of lateral movement significantly.

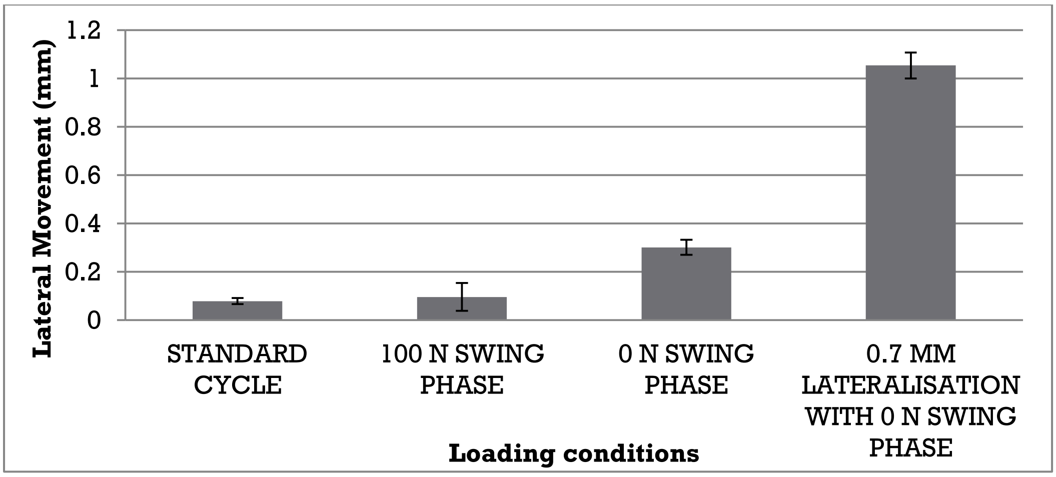


Figure 3:16: Graph showing increasing lateral movement with decreasing swing phase loads and further increase with the lateralisation spring force

The total displacement of the cups was set to 1.0 mm to include the self-alignment of the fixtures equating; to 0.7 mm of medial displacement during swing phase. This was tested over 0.5 million cycles with the movement of 10 consecutive cycles recorded at each point in time. The lateral displacement showed approximately ± 0.2 mm movement from the 1.0 mm displacement set, Figure 3:17. Variability in the lateral movement measured was attributed to the variability in self-aligning of the bearings seen in Figure 3:16.

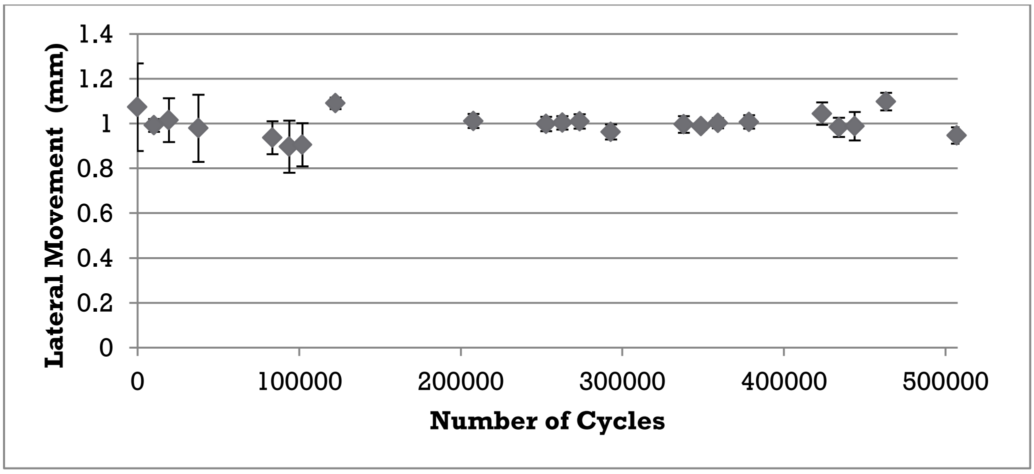


Figure 3:17: Mean lateral displacement (measured over 10 cycles) of the cup over 500000 cycles (± 1 sd)

4 Standard and Adverse Testing of Vitamin-E Blended Highly Crosslinked Polyethylene against Chromium Nitride Coated and Uncoated Metal

4.1 Introduction

Metal–on-polyethylene is the most popular material combination in total hip replacements (Powers-Freeling, 2013) however the wear products from ultra-high molecular weight polyethylene have been shown to lead to bone resorption and loosening of the implant due to osteolysis (Willert et al., 1990). Recently, the inclusion of an anti-oxidant, most commonly vitamin-E, into crosslinked polyethylene has been proposed to maintain low wear rates and minimise the oxidative degradation of the polymer (Bracco and Oral, 2011). Initial tests with this material have shown lower *in vitro* wear rates than conventional polyethylene (Oral et al., 2006, Affatato et al., 2011) and no oxidation under accelerated aging conditions (Rowell et al., 2011) leading to the adoption of this generation of polyethylene by most major orthopaedic device manufactures (Kasser, 2013). Wear testing of this material has predominantly focussed on a small number of studies using small bearings under standard test conditions yet large diameters have been proposed (Oral et al., 2012).

Retrievals of metal-on-polyethylene bearings have reported scratching of metallic heads mainly attributed to third body debris (Tipper et al., 2000), with Ra values as high as 4.2 μm (Kruger et al., 2013) and damage over an area of 25% of retrieved heads (Jasty et al., 1994). This has led to adverse testing of polyethylene focusing roughened conditions, either through direct scratching of the head or the inclusion of third body particles such as bone cement or alumina (Barbour et al., 2000, Bragdon et al., 2003). However, the influence of this scratching on the wear and ionic release from the metal head has not been considered despite reported of elevated blood cobalt levels in patients with metal-on-polyethylene bearings (Savarino et al., 2002).

As roughening of metallic heads has shown to dramatically increase polyethylene wear under walking and jogging conditions (Bowsher and Shelton, 2001), ceramic heads have been proposed due to their scratch resistance (Callaghan and Liu, 2009). Standard simulator studies, however, have shown little improvement in wear of crosslinked polyethlyene with the adoption of a ceramic head (Galvin et al., 2010) although wear reduction is well documented in adverse hip simulator studies incorporating third body abrasives (Wang and Schmidig, 2003).

The use of ceramics has been limited due to historic reports of fracture and can only be safely manufactured to a diameter of 48 mm (Rodriguez and Cooper, 2013). An alternative solution has been the coating of the metal bearing surface with a ceramic, such as titanium nitride, chromium nitride or diamond like carbon. These have been shown to exhibit improved scratch resistance over the uncoated metal, but have had limited success in polyethylene wear reduction due to the increased roughness of the coating even after polishing, resulting in higher wear rates than standard metal-on-polyethylene (Galvin et al., 2010). The potential for these coatings to reduce cobalt release has not been previously investigated in metal-on-polyethylene bearings although has been shown in metal-on-metal testing (Royle, 2012).

In this study, the wear and cobalt release of metal on vitamin-E blended highly crosslinked polyethylene is investigated under a series of test conditions to consider the applicability of this bearing for use in large diameters. The use of a chromium nitride coating on the metallic head is further considered to reduce wear, due to an increased scratch resistance, and reduce cobalt release.

4.2 Materials and Methods

4.2.1 Hip bearings

Sixteen hip bearing couples were tested in this study, four of 28 mm diameter representing bearings in clinical use and twelve prototype 52 mm diameter. Three additional liners; two 52 mm diameter and one 28 mm diameter, were used as unloaded soak controls. All liners were 0.1 wt% vitamin-E blended polyethylene (GUR 1020) crosslinked at 120 kGy and mechanically annealed (Corin, UK), manufactured from pucks. The liners were tested in cobalt chrome shells with the smaller bearings taken from stock and therefore utilising a locking mechanism design commercially available. This mechanism featured notches on the liners which fit into the castellation design of the shells. The larger bearings featured a rosette locking mechanism between the shells and liners, Figure 4:1.

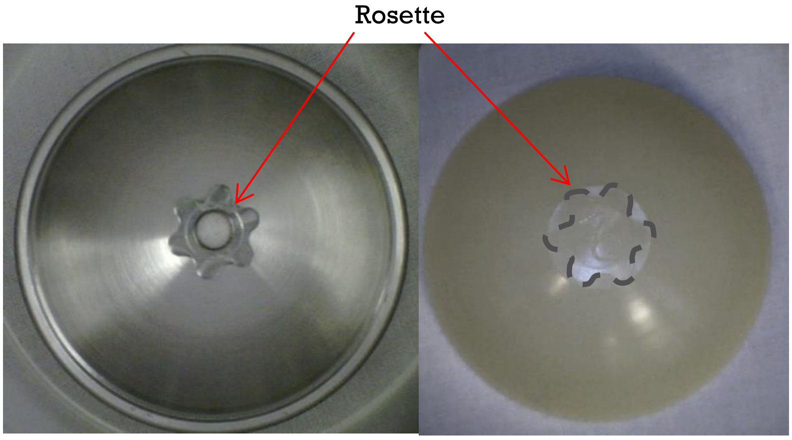


Figure 4:1: Rosette locking mechanism connecting the 52 mm diameter liners with shell

All liners were paired with cast, hot isostatically pressed and solution annealed CoCrMo alloy heads to give clearances of 100-450 μm in the 28 mm diameter bearings and 325-681 μm in the 52 mm diameter bearings. Twelve of these heads remained uncoated while four 52 mm diameter heads of the same metallurgy were coated with chromium nitride (CrN). Coating of the metallic surfaces was performed by Tecvac Ltd (Cambridge, UK) using plasma assisted electron beam physical vapour deposition (EBPVD) to a thickness of approximately 3-7 μm. Bearings were suspended in the coating chamber on a wire carousal above the coating source located in the centre, Figure 4:2. To ensure consistency of the coatings, they were rotated during this process. These heads were polished to remove microdroplets formed on the surface due to the coating method to give low surface roughness of the heads, Table 4:1, measured using optical surface profilometry as described in section 4.2.5.

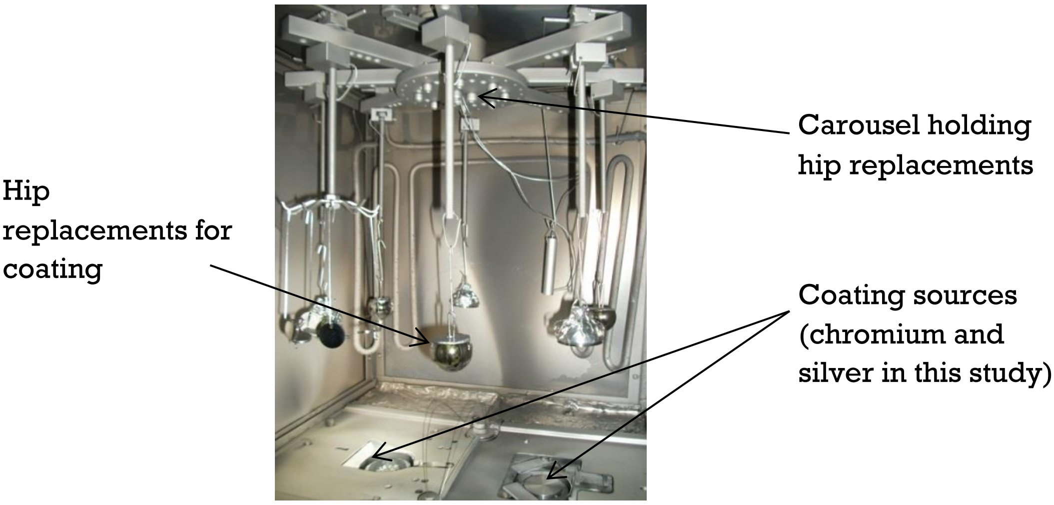


Figure 4:2: Inside of the coating chamber in which hip replacements are coated using electron beam physical vapour deposition

Table 4:1: Average surface roughness, Ra, average maximum profile height, Rz, and range of profile height, Rt, for heads before testing showing low surface roughness achieved in the coatings following polishing

Head	Ra, μm (± 1 sd)	Rz, μm (± 1 sd)	Rt, μm (± 1 sd)
28 mm uncoated metal	0.03 (± 0.01)	2.66 (± 0.69)	4.08 (± 1.97)
52 mm uncoated metal	0.02 (± 0.01)	1.65 (± 0.72)	2.77 (± 1.01)
52 mm CrN coated (unpolished)	0.02 (± 0.01)	1.26 (± 0.41)	3.62 (± 0.74)
52 mm CrN coated (polished)	0.01 (± 0.01)	0.91 (± 0.52)	1.30 (± 0.84)

The liners were pre-soaked in pure deionised water for a minimum of 53 days, Table 4:2. The 52 mm diameter bearings were divided into long (606 days) and short (53 days) soak durations. The 28 mm diameter liners were soaked for 84 days compared to the standard 28 mm diameter polyethylene liner crosslinked at 50 kGy (DePuy, UK) soaked for 79 days.

Table 4:2: Soak duration and mass gain of different polyethylene liners before testing

Polyethylene Liner	Number of liners	Soak duration, days	Percentage mass gain absorbed before testing
28 mm crosslinked	1	73	0.02 ± 0
28 mm Vitamin-E crosslinked	5	84	0.01 ± 0.001
52 mm Vitamin-E crosslinked (short soak)	9	53	0.01 ± 0.001
52 mm Vitamin-E crosslinked (long soak)	5	606	0.02 ± 0.001

The short soak 52 mm diameter liners initially absorbed the greatest amount of water relative to their initial weight but after 25 days, little difference was observed between these and the smaller diameter vitamin-E containing bearings, Figure 4:3. The inclusion of vitamin-E appeared to reduce the amount of water absorbed by the liners throughout soaking although crosslink density and other manufacturing differences may also have influenced this.

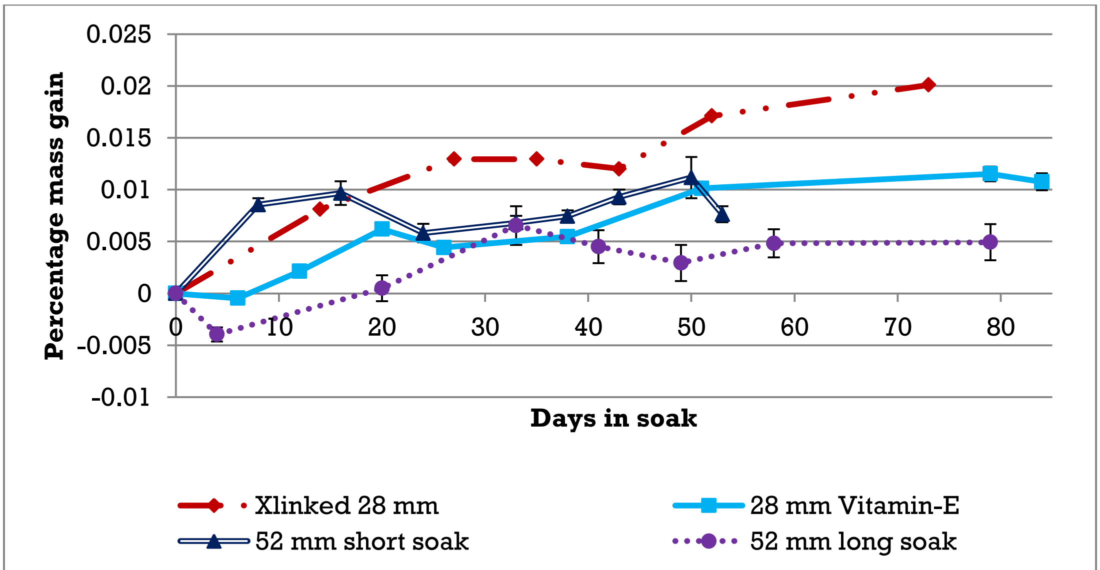


Figure 4:3: Mean percentage (±1 sd) of mass gain in liners over the first 80 days of soaking

The long soak liners appeared to take up water more slowly than the other liners over the initial 80 days, but when left undisturbed for 432 days substantial absorption was observed, Figure 4:4. Fluid uptake continued until 570 days when this appeared to settle. The increased soak duration of these liners resulted in 2.3 fold increase in mass gain compared to the short soak liners.

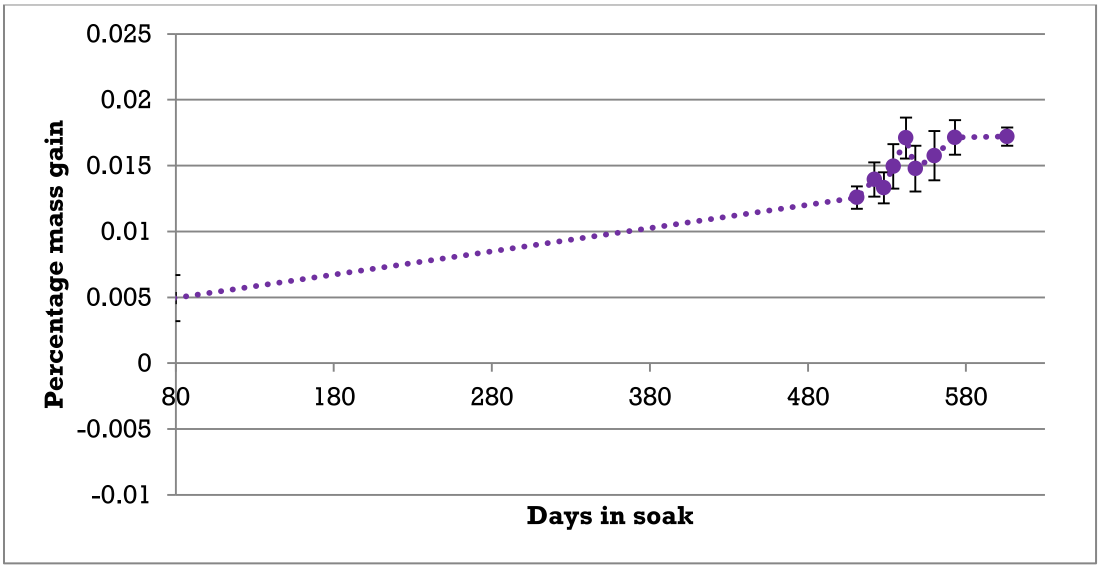


Figure 4:4: Mean percentage (±1 sd) of mass gain of long soak liners from 80 days to 606 days

4.2.2 Test conditions

All tests were conducted in an eight station orbital hip simulator (MTS Systems, USA) as described in Table 4:3. In the small diameter bearings and the long term soak metal-on-polyethylene bearings, one million cycles of standard testing as described in section 3.1.1 (Standard testing) following ISO 14242-3:2009 were performed. In the short soak 52 mm liners, paired with CrN coated and uncoated heads, five million cycles of this testing was conducted. Standard test conditions were followed by one million cycles with third body particles added to the test fluid. In the bearings tested to 1 million cycles, 5 mg/mL of bone cement powder (Simplex P, Stryker Ltd, USA) of mode sizes 1.7825 and 24.606 μm was added to the test fluid. The remaining bearings were tested with the introduction of 0.15 mg/mL of alumina particles of mode sizes 0.778 and 3.0975 μm, described in section 3.1.2. One million cycles of further standard testing (with the removal of third body particles) was subsequently conducted in all bearings. Those tested with alumina as a third body were then subjected to three jogging intervals of 14,400 cycles at speeds of 1, 1.5 and 1.75 Hz; slow, medium and fast respectively as described by Bowsher and Shelton (2001) and section 3.1.3.

Table 4:3: Test conditions of all polyethylene bearings

Bearings	Test Conditions	Duration, x 10^6 cycles
4 x 28 mm MoP	Standard	1
	3rd body [bone cement]	1
	Standard/roughened	1
4 x 52 mm MoP (long soak)	Standard	1
	3rd body [bone cement]	1
	Standard/roughened	1
4 x 52 mm MoP (short soak)	Standard	5
	3rd body [alumina]	1
	Standard/roughened	1
	Jogging	3 x 0.0144
4 x 52 mm CrNoP	Standard	5
	3rd body [alumina]	1
	Standard/roughened	1
	Jogging	3 x 0.0144

Gravimetric wear calculations were conducted every third of a million cycles in the initial million cycles and every million cycles thereafter except for during simulated jogging in which wear was determined after each interval. Components were cleaned and weighed and their volume loss determined from their mass loss and densities of 8300 kg/m^3, 5900 kg/m^3 and 942 kg/m^3 for CoCrMo metal, CrN and polyethylene respectively. Gain observed in the polyethylene soak controls was removed from wear results.

4.2.3 Particle isolation

Fluid samples taken at 1.00 mc and after jogging intervals were used to analyse polyethylene particles. The protocol used was adapted from Billi et al. (2011a) and is described in detail in Appendix B. Briefly, 3 mL of fluid was taken and the proteins digested over a period of 4 days with the addition of urea, HEPES, sodium azide and Proteinase K. The fluid was subsequently sonicated to disperse particles and layered below concentrations of urea and sodium lauroyl sarcosine, urea, EDTA, HEPES and sodium azide into centrifuge tubes. These were spun for 4 hours at 284,000 *g* using a SW 41 Ti rotor (Beckman Coulter USA) allowing the particles to separate to the top of the tube. These were then placed below a concentration gradient of propan-2-ol and spun for 30 minutes at 5000 *g* followed by 4 hours at 284,000 *g*. The final purification step again used propan-2-ol, this time at concentrations of 10 and 50% placed below the particle containing fluid and spun at 284,000 *g*. After each centrifugation the particles collected together to form an opaque layer in the tube which was removed.

The polyethylene particles were spun onto a silicon wafer using a MLS-50 rotor at a speed of 84,000 *g* for 4 hours. The silicon wafer was removed and allowed to dry before being mounted to SEM pin studs and gold coated to observe via scanning electron microscope (JEOL, Japan). These were imaged at an accelerating voltage of 5 keV and a working distance of 10 mm. Five different areas of each silicon wafer were viewed with a minimum of 3 images taken from each area to give a minimum of 250 particles. Images of the particles were quantified using Image Pro Plus (Media Cybernetics, USA). The contrast of the images was increased to allow the program to count the number of particles and their size which was reported as the maximum Feret's diameter, d_{max}.

4.2.4 Cobalt release

Fifteen millilitres of fluid was taken from each station at approximately 3, 6, 12 and 24 hours, correlating to 10,800, 21,600, 43,200, 86,400 cycles respectively, as well as at every gravimetric measurement interval and fluid change in hip simulator to analyse the total (ion plus particles) cobalt concentration. These were analysed using graphite furnace atomic absorption spectrometry, GFAAS, (SpectrAA 220FS atomic absorption spectrometer with a GTA-110 autosampler and deuterium background correction source [D2 b.c.], Varian, Oxfordshire, UK). This technique vaporises a sample and measures the concentration of an element by the amount of absorption of a specific wavelength experienced, specific to the element of interest (Butcher and Sneddon, 1998).

The system was controlled using SpectraAA version 4.10 PRO software and underwent a thermal method of drying, ashing, atomisation and cleaning, using pyrolytic carbon coated graphite partition tubes (Royle, 2012), Figure 4:5.

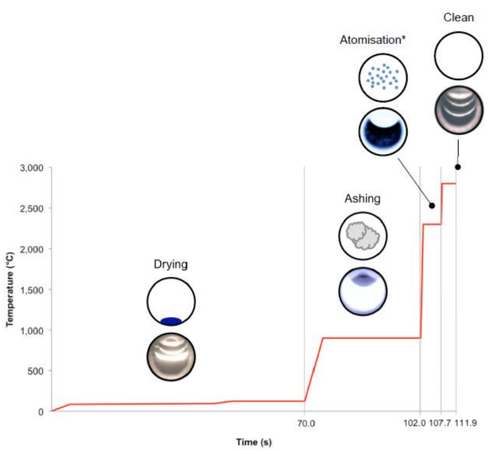


Figure 4:5: Thermal method used for GFAAS analysis comprising of drying, ashing atomisation and cleaning stages. Taken from Royle (2012)

Fifteen millilitres of the fluid samples taken at 0.67 million cycles was spun for 3 hours at 164,000 *g* using a 70 Ti rotor (Beckman Coulter, USA). This allowed for any particles produced to sediment at the bottom of the tube and the supernatant removed was used to determine the ionic cobalt concentration. It was assumed that all particles had been spun to the bottom of the centrifuge tube based on work by Lu et al (2012).

Diluted serum (with no wear particles) was added to solutions of known concentration created with a master stock of 100 mg/L (Merck KGaA, Darmstadt, Germany). The absorption of these known concentrations was recorded to create a calibration curve. The absorption of samples from the test fluid was recorded against this curve to give the concentration of cobalt. Each sample was measured twice and the relative standard deviation between these concentrations recorded; if this was greater than 5%, a third measurement was taken and the mean reported.

4.2.5 Surface analysis

Before and after each test, the surface roughness of the femoral heads were measured using an optical surface profilometer (Bruker, USA). The heads were measured using a green light, narrow band filter with 10 µm back scanning and a cut off of 0.08 µm. A 20 x lens was used to provide the highest resolution possible over an area of approximately 0.26 mm^2. Five measurements in total were taken for each head; one at the apex of the head and four with the head at 35° in the 52 mm heads and 12° in the 28 mm heads positioned on a V-block, Figure 4:6, rotated at approximately 90°. The surfaces were corrected for spherical shape, with average surface roughness, Ra, average peak to valley roughness, Rz, and the maximum peak to valley roughness, Rt, recorded.

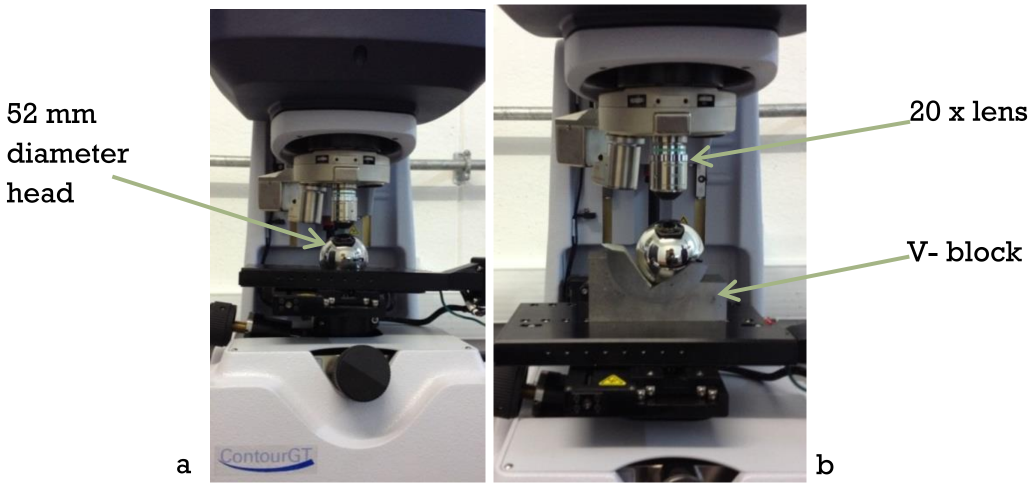


Figure 4:6: Set up for surface roughness measurement of the 52 mm heads (a) at the apex of the head and (b) at 35° on a V-block

Scanning electron microscope (Inspect F, FEI, Eindhoven, NL) images of the head surfaces were taken before and after tests by placing the heads on a custom made fixture. These were imaged at 20.0 keV and a working distance of 10 mm. All heads and cups were imaged using an USB optical microscope (VMS-004 Discovery Series 400x, Veho, Hampshire, UK). These were placed on lint free wipes and placed in a nylon tube covered with white paper to prevent reflections. The cups were imaged in a similar fashion but the wear areas were also imaged at a higher magnification.

4.3 Results

4.3.1 28 and 52 mm diameter metal-on-polyethylene under standard conditions

The 28 mm diameter liners impinged on the head fixtures resulting in the removal of material from the edge of the liner. Wear was corrected for this volume loss due to impingement (full details in Appendix C). Polyethylene wear of the 28 mm diameter bearings was less than for large diameter bearings, Figure 4:7.

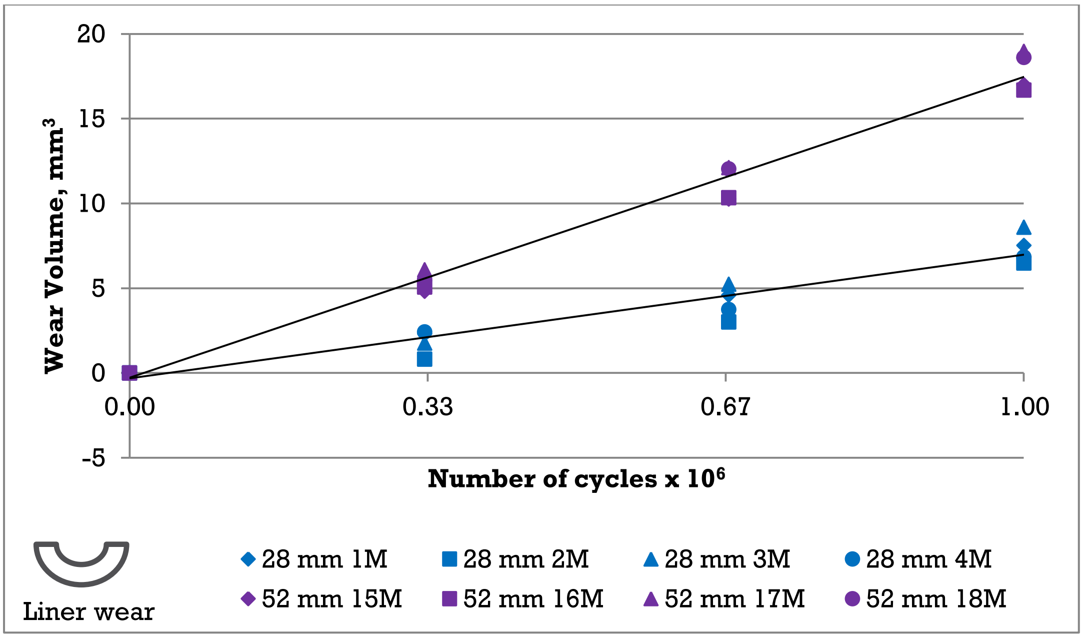


Figure 4:7: Individual cumulative volume loss of 28 mm (blue) and 52 mm (purple) diameter polyethylene liners after 1 million cycles of standard testing with linear fit for each bearing size

No run-in of polyethylene wear was observed in either bearing diameter allowing steady state wear rates to be determined, Table 4:4. This showed a significant ($p<0.01$) 2.4 fold increase in wear rate with increased diameter.

Table 4:4: Increasing mean steady state wear rates of polyethylene liners with diameter under standard conditions

Bearing	Wear rate, mm^3/mc (± 1 sd)
28 mm MoP	7.37 ± 1.05
52 mm MoP (long soak)	17.74 ± 1.18

Despite the increased wear rate with the larger diameter, no difference was observed in the polyethylene wear behaviour of bearings. Both liners showed the removal of machining marks after 1 million cycles under standard conditions, Figure 4:8. Within the wear patches of the liners, fine multidirectional scratches were generated.

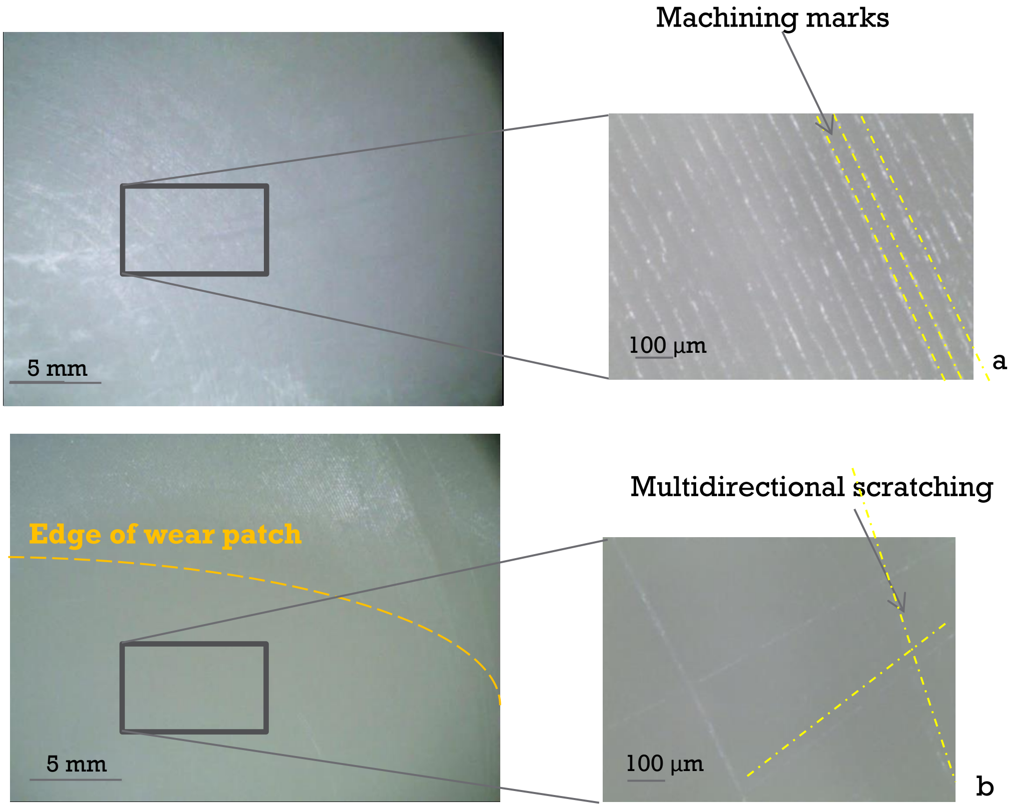
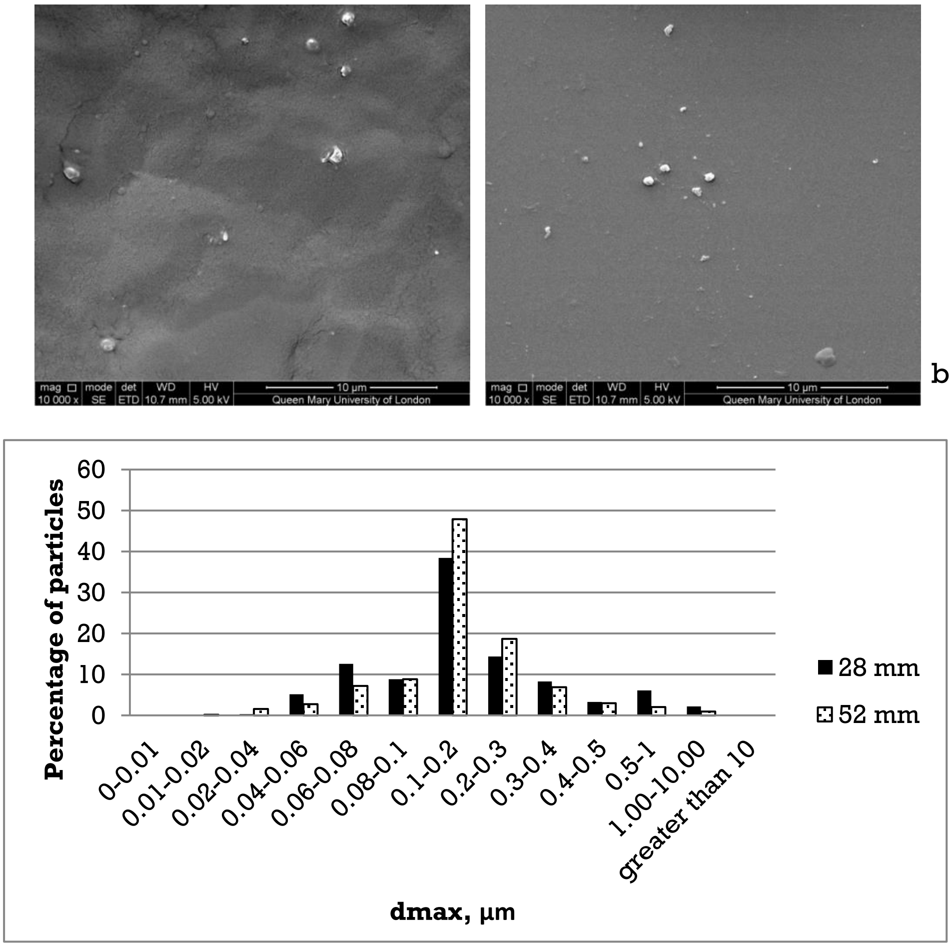


Figure 4:8: 52 mm diameter polyethylene liner (a) before and (b) after 1 million cycles of standard testing showing the removal of machining marks and the generation of scratches

The polyethylene particles generated in the bearings were similar showing small, spherical shaped particles, Figure 4:9. The majoirty of particles generated from both diameters were of the size 0.1-0.2 µm. Although the results appeared to show larger particles generated in the 52 mm diameter bearings, no significant difference was observed between diameters with modes of 0.15 and 0.16 µm in the 28 and 52 mm diameter bearings respectively.

a

b



c

Figure 4:9:Predominantly spherical polyethylene particles generated in (a) 28 mm and (b) 52 mm diameter bearings and (c) the resulting particle distribution based on a minimum of 250 particles in both metal-on-polyethylene bearings after 1 million cycles of standard testing

Mass loss, and therefore, volume loss was also recorded in the large diameter metal heads with an initial run-in phase up to a third of a million cycles, Table 4:5. Following this, a significant ($p<0.01$) reduction in the measured volume loss was observed showing a decrease in wear rate at each gravimetric interval, Figure 4:10. The 28 mm diameter heads produced only small amounts of mass loss, within the lower limits measurable gravimetrically; therefore volume loss during the one million cycles of standard testing was unmeasurable. The run-in wear rates for the 52 mm diameter metal heads was significantly ($p<0.01$) greater than the 28 mm diameter heads but no significance (p>0.05) was observed after this.

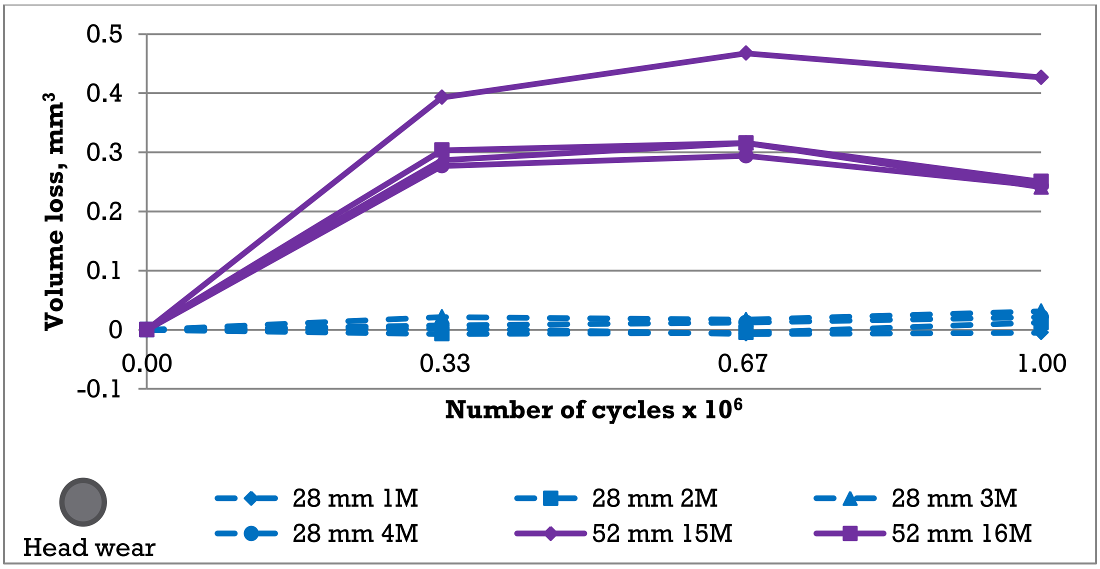


Figure 4:10: Individual cumulative volume loss of large (solid) and small (dashed) diameter metal heads over 1 million cycles of standard testing

Table 4:5: Mean run-in (0-0.33 mc) and transition (0.33-1.00 mc) wear rates of the heads under standard test conditions in metal-on-polyethylene bearings

Bearing	**Run-in wear rate mm^3/mc (± 1sd)**	**Transition wear rate, mm^3/mc (± 1sd)**
28 mm MoP	0.02 ± 0.04	-0.01 ± 0.07
52 mm MoP (long soak)	0.96 ± 0.16	0.04 ± 0.06

Although wear was measured in the large diameter heads, no significant difference (p>0.05) was observed in the surface roughness parameter before and after testing. The smaller diameter bearings appeared smoother with lower Rt and Rz of 2.91 ± 0.88 μm and 1.86 ± 0.78 μm respectively (p<0.01). Scratching on both head diameters was observed under scanning electron microscopy, Figure 4:11, which was thicker than those seen from machining the heads, suggesting that wear may have occurred on these heads.

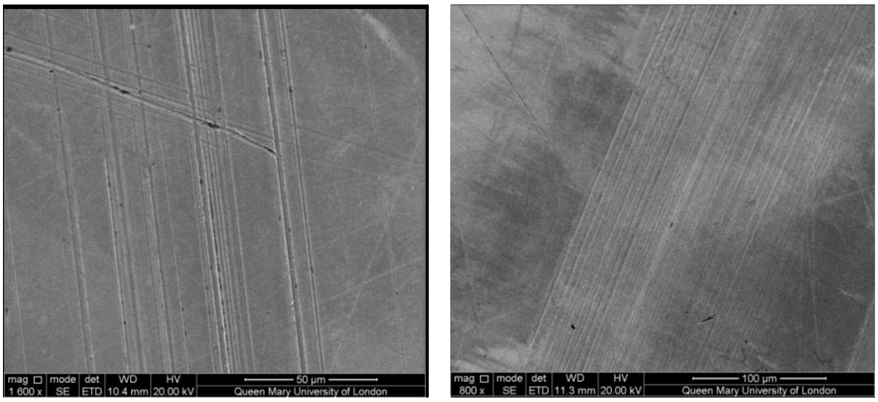
a  b

Figure 4:11: Scanning electron microscopy images of (a) 28 mm and (b) 52 mm diameter heads showing scratching after 1 million cycles of standard testing against polyethylene liners

Cobalt release was measurable in all bearings, Figure 4:12. In keeping with the gravimetric reading, greater amounts were measured in the 52 mm diameter MoP bearings (123 ± 74 ppb after 1 million cycles) than the 28 mm diameter bearings (51 ± 8 ppb after 1 million cycles). However, the smaller diameter produced greater levels of cobalt compared to the soak controls (17 ppb) indicating that cobalt was being released as a result of the wear process. Spinning of this fluid showed 80% of this cobalt in both cases to be ionic. This high ionic content and low cobalt release resulted in difficulty observing any metal wear particles with approximately only 0.1 μg of particles obtained after spinning.

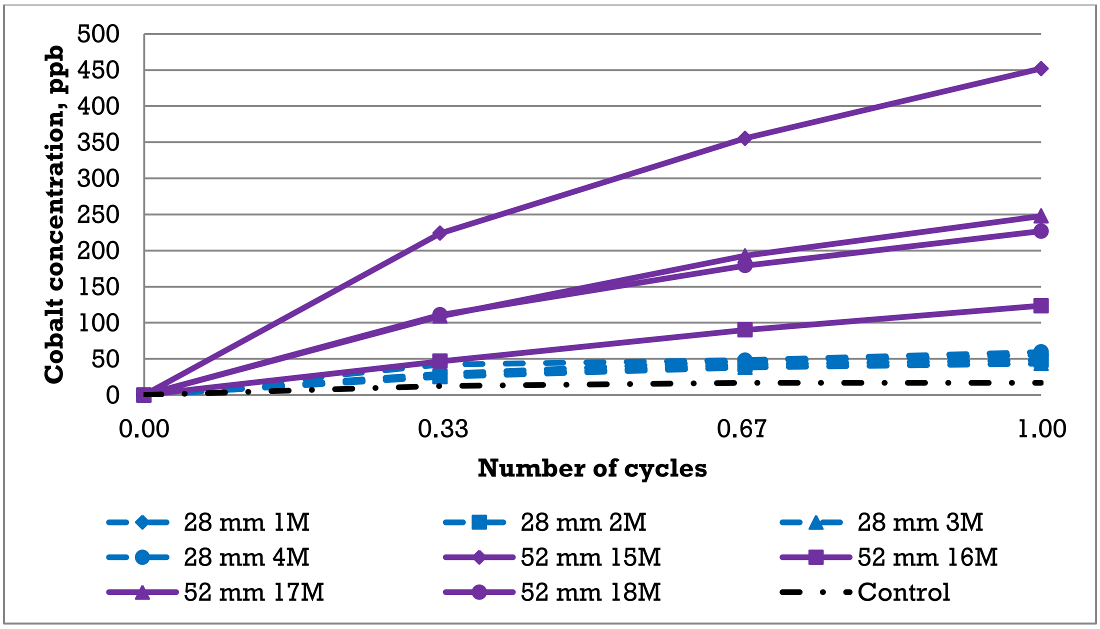


Figure 4:12: Cumulative cobalt released during 1 million cycles of standard testing in 52 mm and 28 mm diameter metal on polyethylene bearings

In the large diameter bearings, cobalt levels were measurable as early as 10,800 cycles (3 hours), Figure 4:13. This rate of release at this point was high and showed a deceleration in cobalt release as testing continued. In the 28 mm diameters, cobalt could not be measured until after 86,400 cycles (24 hours).

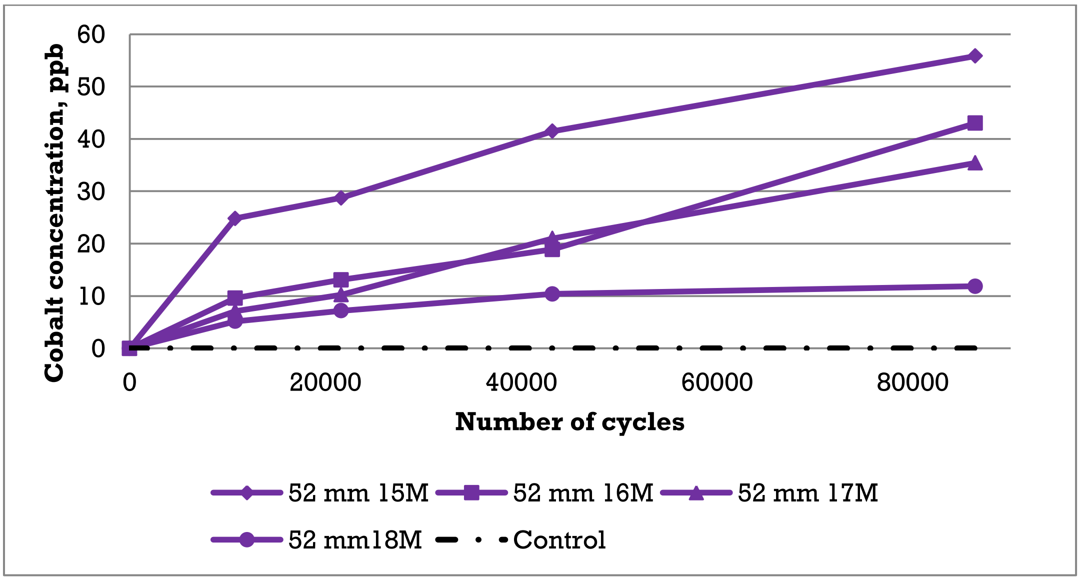


Figure 4:13: Increasing cobalt released over the first 24 hours (86400 cycles) in 52 mm diameter metal-on-polyethylene bearings

4.3.2 28 and 52 mm diameter metal-on-polyethylene under adverse conditions

Bone cement, added to the test fluid for 1 million cycles, increased the wear rate in both diameter bearings, Figure 4:14. It was found that the inclusion of third body particles produced a similar wear rate regardless of diameter during the initial third of a million cycles but the smaller bearings appeared to recover with time resulting in both wear rates doubling after 1 million cycles compared to standard conditions ($p<0.01$), Table 4:6.

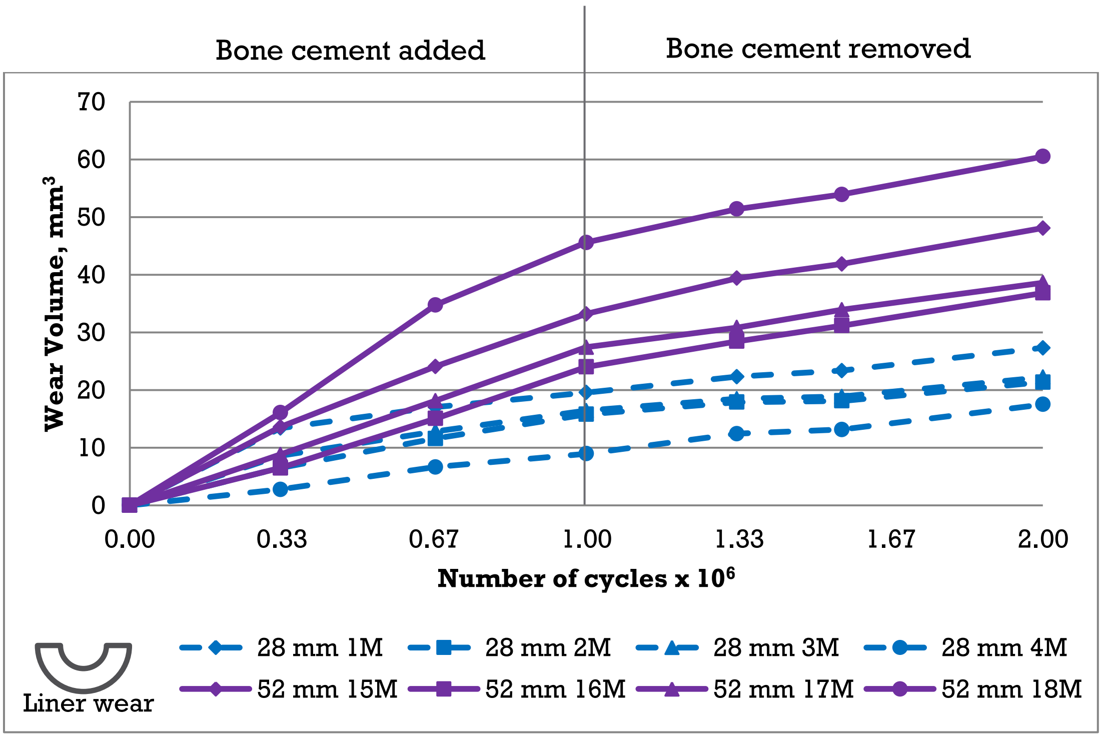


Figure 4:14: Increased polyethylene wear of 28 mm and 52 mm diameter bearings tested for 1 million cycles with bone cement added to the test fluid and a wear reduction during a further 1 million cycles with the third body particles removed

The removal of the bone cement particles saw the polyethylene wear reduce to wear rates of 6.56 ± 1.40 and 13.33 ± 1.61 mm^3/mc in 28 and 52 mm diameter bearings respectively. These rates were lower than in the initial standard conditions but this was only significant ($p<0.01$) in the 52 mm diameter liners.

The wear rates of both diameters were, however, significantly ($p<0.01$) lower than the wear rates when tested with bone cement.

Table 4:6: Mean polyethylene wear rates (±1sd) and percentage increase from standard test conditions for bearings under bone cement third body conditions and mean wear rate with bone cement particles removed

Bearing	Wear rate under third body conditions, mm^3/mc	% increase from standard wear rate	Wear rate with third body particles removed, mm^3/mc
28 mm MoP	14.87 ± 4.01	202	6.56 ± 1.40
52 mm MoP (long soak)	32.76 ± 9.90	184	13.33 ± 1.61

The bone cement third bodies created more scratches on the liners, Figure 4:15. These scratches remained fine, with some embedding of the bone cement in the polyethylene observed. These appeared to wear away with continued testing without bone cement in the test fluid.

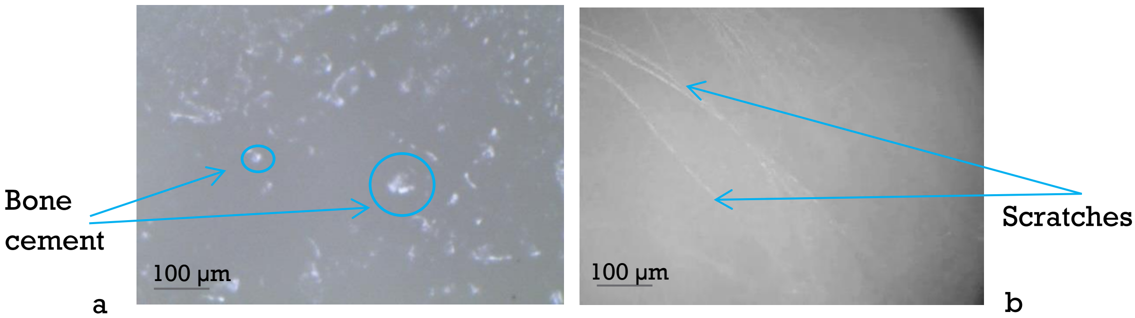


Figure 4:15: Liners showing (a) embedding of bone cement particles and (b) scratching caused during third body test conditions

The polyethylene particles generated during testing with bone cement still showed the majority of particles sized between 0.1-0.2 µm, Figure 4:16c, with modes of 0.13 and 0.14 µm in the 28 and 52 mm diameters respectively. These particles were still spherical in shape, Figure 4:16a and b, but a greater number of particles were sized between 0.2-0.3 µm in the 52 mm diameter bearings than the 28 mm diameter bearings. No change was observed in the particle distribution when bone cement particles were removed from the test fluid with modes of 0.13 and 0.14 μm in the 28 and 52 mm diameter bearings respectively.

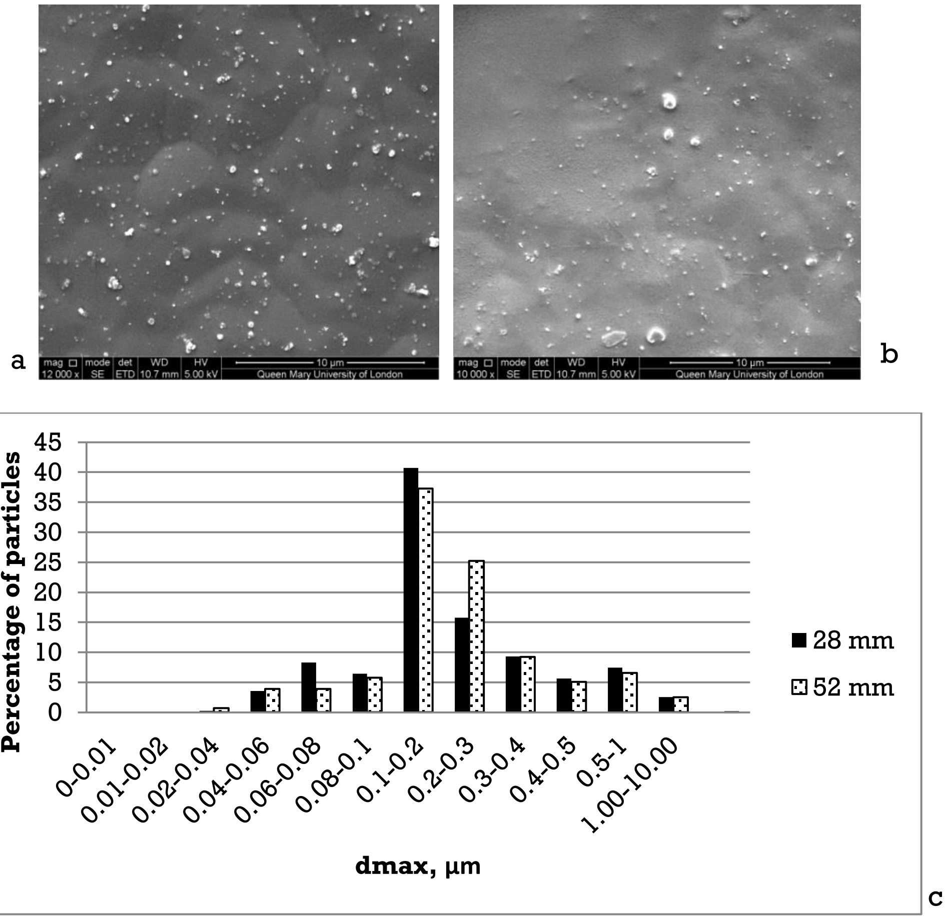


Figure 4:16: Polyethylene wear particles produced under bone cement third body conditions in (a) 28 mm diameter and (b) 52 mm diameter bearings and (c) the resulting particle distribution

During testing with bone cement particles, the small diameter bearings showed little change in head volume change, Figure 4:17. The large diameter heads varied with mass gain reported during the first and final thirds of a million cycles, possibly due to adhesion of bone cement onto the heads resulting in difficulty determining wear gravimetrically. The removal of the bone cement particles resulted in measurable volume loss in the large diameter bearings, most noticeable between 0.33 and 0.67 mc. This may have been the result of removal of the bone cement adhered to the surface. The small diameter bearings, again showed little change in head volume.

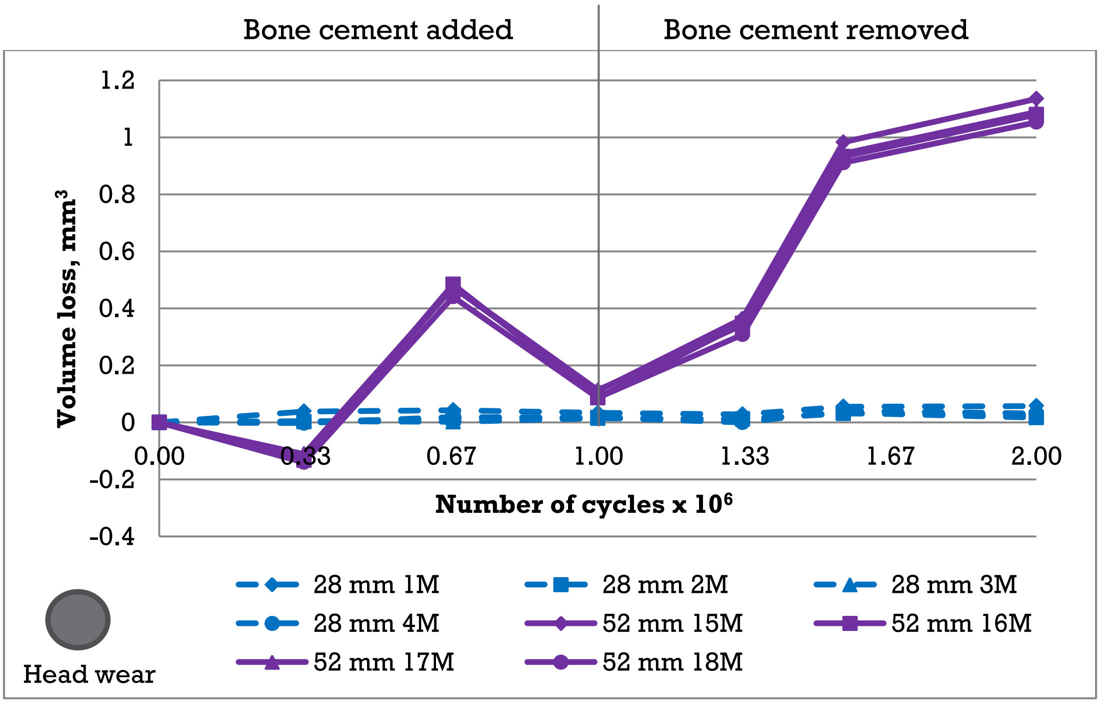


Figure 4:17: Individual volume loss of 28 mm and 52 mm heads over 1 million cycles of testing with bone cement particles added to the test fluid and 1 million cycles with these particles removed

Evidence of adhesion of the bone cement contaminants to the heads was observed under scanning electron microscopy after 1 million cycles of third body testing, Figure 4:18. This adhesion was observed in both diameters despite mass gain was only being measured in the larger diameters. The majority of these contaminants were removed during the 1 million cycles of further testing in clean lubricant.

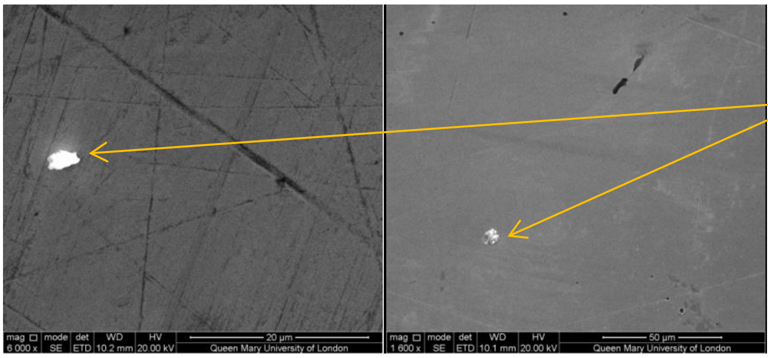


Figure 4:18: Scanning electron microscope images of (a) a 28 mm diameter head and (b) a 52 mm diameter head showing bone cement (white) embedding into the surface of the heads after testing

The adhesion of the bone cement onto the heads did not result in a significant difference (p>0.05) in the roughness of the metal heads before and after bone cement testing, Table 4:7. After 3 million cycles of testing (i.e. a further 1 million cycles of testing in a clean lubricant) no significant difference (p>0.05) was observed in any roughness parameter of the heads compared to earlier stages of testing.

Table 4:7: Little difference in the average surface roughness of the heads before (1 mc) and after (2 mc) bone cement third body testing and after one million cycles of testing in clean test fluid after this (3 mc)

Head	**Time point**	**Ra, μm (± 1 sd)**	**Rz, μm (± 1 sd)**	**Rt, μm (± 1 sd)**
28 mm uncoated metal	After 1mc	0.03 ± 0.01	1.86 ± 0.78	2.91 ± 0.88
	After 2 mc (bone cement)	0.03 ± 0.01	1.80 ± 0.65	2.80 ± 0.92
	After 3 mc	0.03 ± 0.01	1.74 ± 0.66	2.72 ± 0.88
52 mm uncoated metal	After 1mc	0.02 ± 0.01	1.59 ± 0.70	2.71 ± 0.94
	After 2 mc (bone cement)	0.02 ± 0.01	1.82 ± 0.73	2.86 ± 0.89
	After 3 mc	0.02 ± 0.01	1.84 ± 0.81	3.04 ± 1.06

Despite difficulties measuring head wear gravimetrically, cobalt release was measurable throughout testing in the large diameter bearings, Figure 4:19. After

1 million cycles of testing with bone cement particles added, the 52 mm diameter bearings produced 4 times more cobalt than the 28 mm diameter; 592 ± 205 and 148 ± 14 ppb. This test condition increased the cobalt release by 4.8 times in both bearings compared to that observed under standard testing. This was statistically significant in both the 28 mm diameter ($p<0.01$) and 52 mm diameter bearings ($p<0.02$). The removal of these particles still produced elevated cobalt levels compared to standard conditions (188 ± 20 ppb compared to 123 ± 74 ppb) in the large diameter bearings. However, this increase was not statistically significant ($p>0.05$) supporting the theory that the increased wear in the heads measured during this test condition signified the removal of bone cement as opposed to metal removal. In the 28 mm diameter bearings, less cobalt was measured with the removal of third body particles than during standard conditions (14 ± 4 ppb compared to 31 ± 8 ppb) which was statistically significant ($p<0.01$).

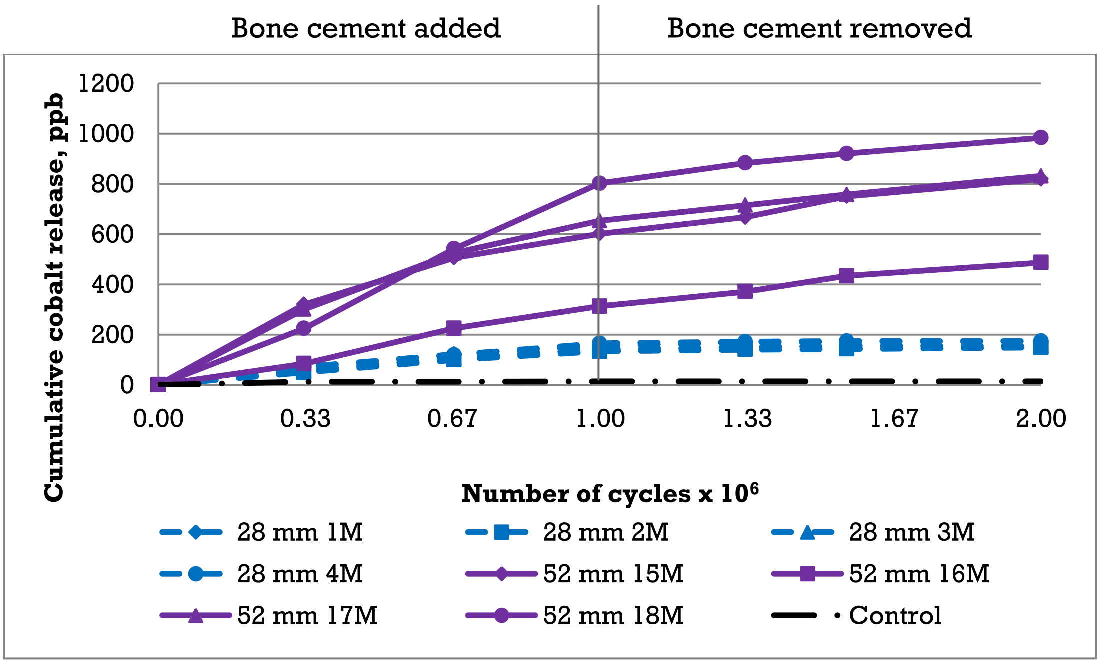


Figure 4:19: Cumulative cobalt release during 1 million cycles of third body bone cement testing and a reduction in cobalt with a further 1 million cycles of clean testing

4.3.3 CrN coated and uncoated metal-on-polyethylene under standard conditions

Under standard conditions, no difference was observed in the polyethylene wear of 52 mm diameter bearings paired with CrN coated or uncoated heads, Figure 4:20. However, this wear rate was approximately twofold lower that than reported in the 52 mm diameter metal-on-long soak polyethylene bearings in section 4.3.1. There was no statistically significant ($p>0.05$) difference in the wear rates of the uncoated and CrN coated bearings with wear rates of 10.63 ± 1.65 mm^3/mc and 9.50 ± 1.18 mm^3/mc respectively, yet these rates were significantly ($p<0.01$) less than the long soak 52 mm diameter liners.

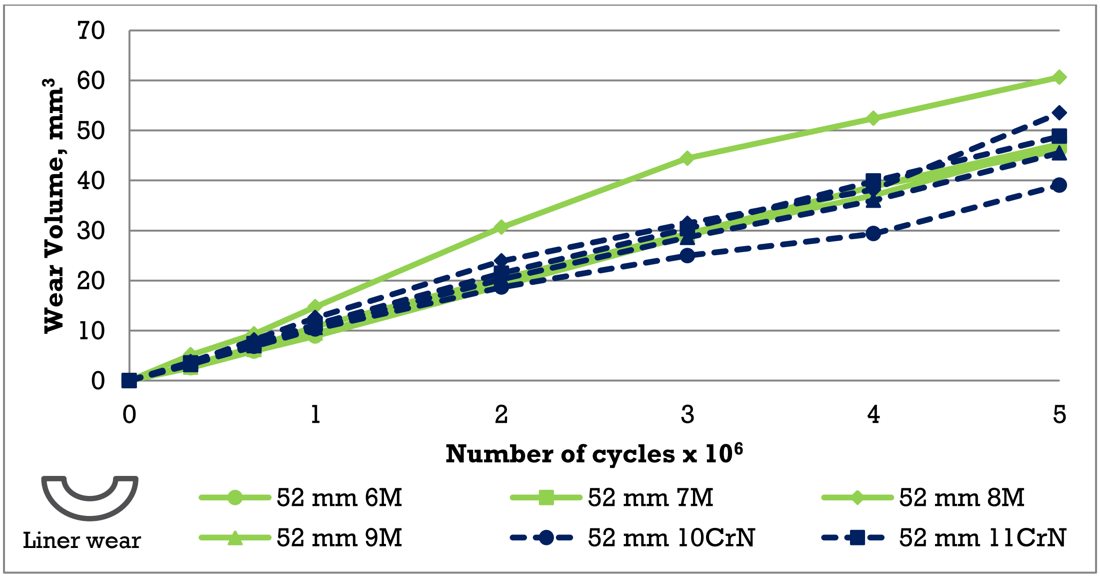


Figure 4:20: Cumulative polyethylene gravimetric wear volume for short term soaked 52 mm diameter polyethylene liners paired with metal heads (solid) and CrN coated heads (dashed)

Despite the decreased wear rate to that observed in the long soak 52 mm diameter liners, the liners showed similar light scratching in the wear patches of the liners. The particles produced in the uncoated metal-on-polyethylene were similar to those produced in the other bearings with a mode of 0.13 μm, Figure 4:21. The CrN coating produced larger particles, yet the majority remained between 0.1 and 0.2 μm with a mode of 0.17 μm.

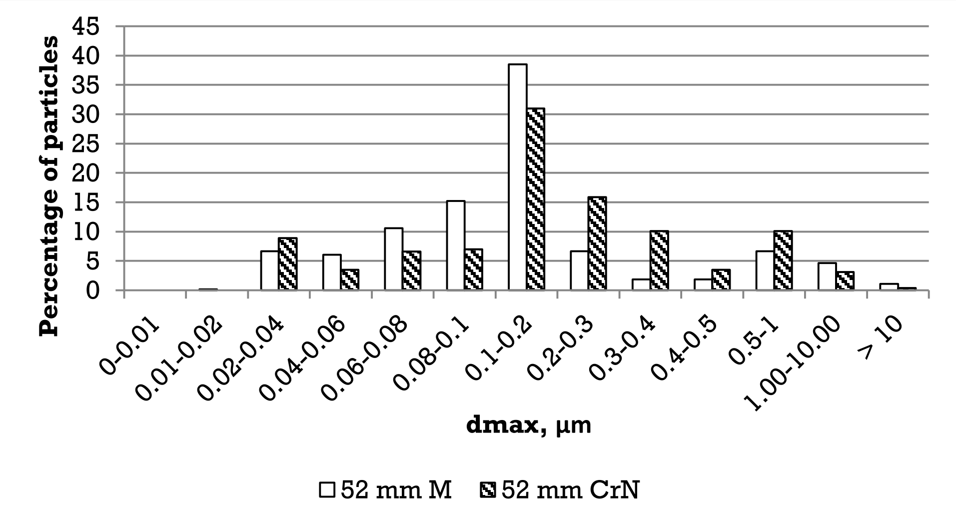


Figure 4:21: Polyethylene particle distribution produced after 1 million cycles of standard testing against CrN coated and uncoated metal

Over the first million cycles of testing, the wear in both heads was measurable, Figure 4:22. However, after one million cycles, mass gain was reported after this due to deposition of protein on the heads and wear was not measureable, Figure 4:23. This gain was greater in the coated than uncoated metal heads.

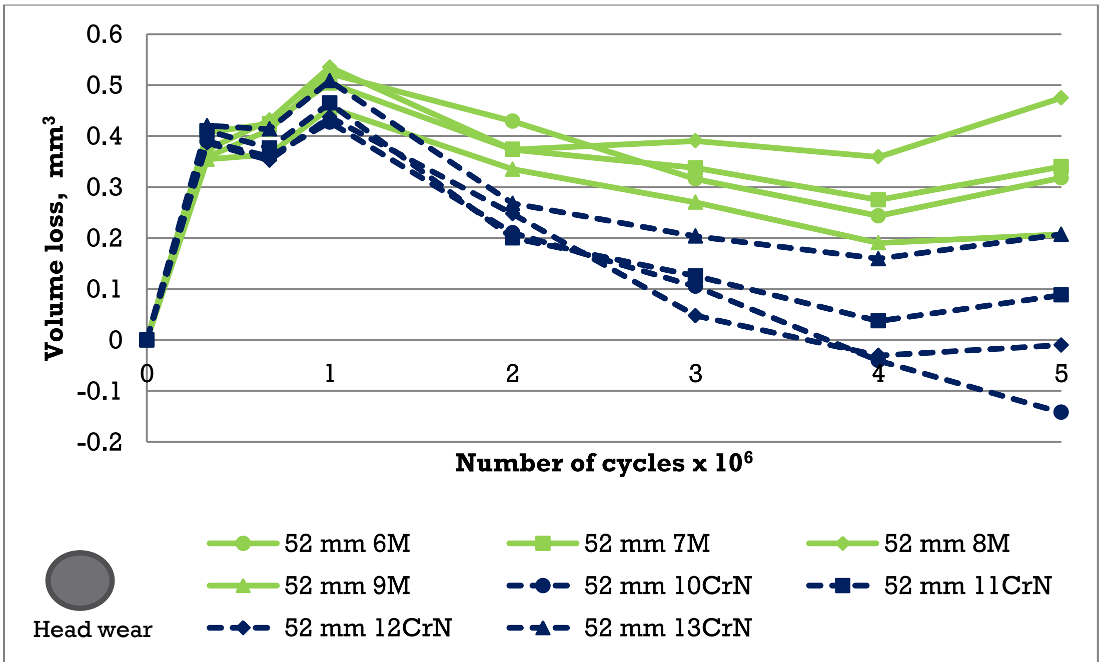


Figure 4:22: Cumulative gravimetric wear of 52 mm CrN coated (dashed) and uncoated (solid) heads over 5 million cycles of testing

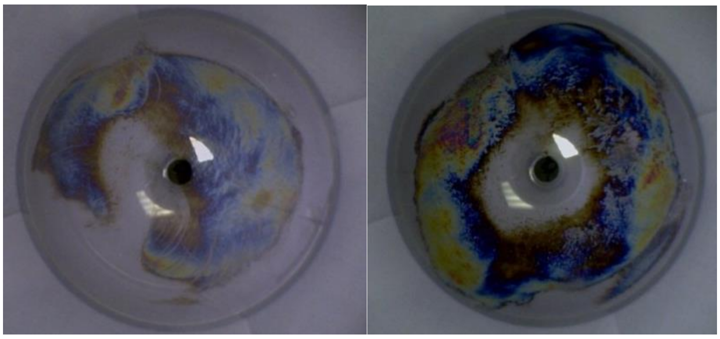
a  b

Figure 4:23: Deposition on the 52 mm diameter (a) uncoated and (b) coated heads after 2 million cycles of hip simulator testing

During the run-in phase of wear (0-0.33 million cycles) no significant ($p>0.05$) difference was observed between heads, Table 4:8. Significant ($p<0.01$) difference was observed in the transition (0.33-1.00 million cycles) wear rates with the uncoated metal heads producing double the wear. Both heads showed significantly ($p< 0.05$) increased head wear over 1 million cycles compared to the long soak 52 mm diameter polyethylene in both wear phases.

Table 4:8: Average run-in (0-0.33 mc) and transition (0.33-1.00 mc) wear rates of the heads under standard test conditions in CrN coated and uncoated metal-on-polyethylene bearings

Bearing	**Run-in wear rate mm^3/mc (± 1 sd)**	**Transition wear rate, mm^3/mc (± 1 sd)**
52 mm MoP (short soak)	1.13 ± 0.09	0.20 ± 0.06
52 mm CrNoP	1.21 ± 0.05	0.09 ± 0.03

Cobalt release was measured throughout all 5 million cycles in the uncoated metal-on-polyethylene bearings. The first million cycles produced statistically similar ($p>0.05$) levels of cobalt to the long soak 52 mm diameter metal-on-polyethylene bearings and showed the release rate of cobalt to reduce after this. At all times, the CrN coating only released cobalt to the same extent as the soak control suggesting the CrN coating was acting as a cobalt barrier, Figure 4:24.

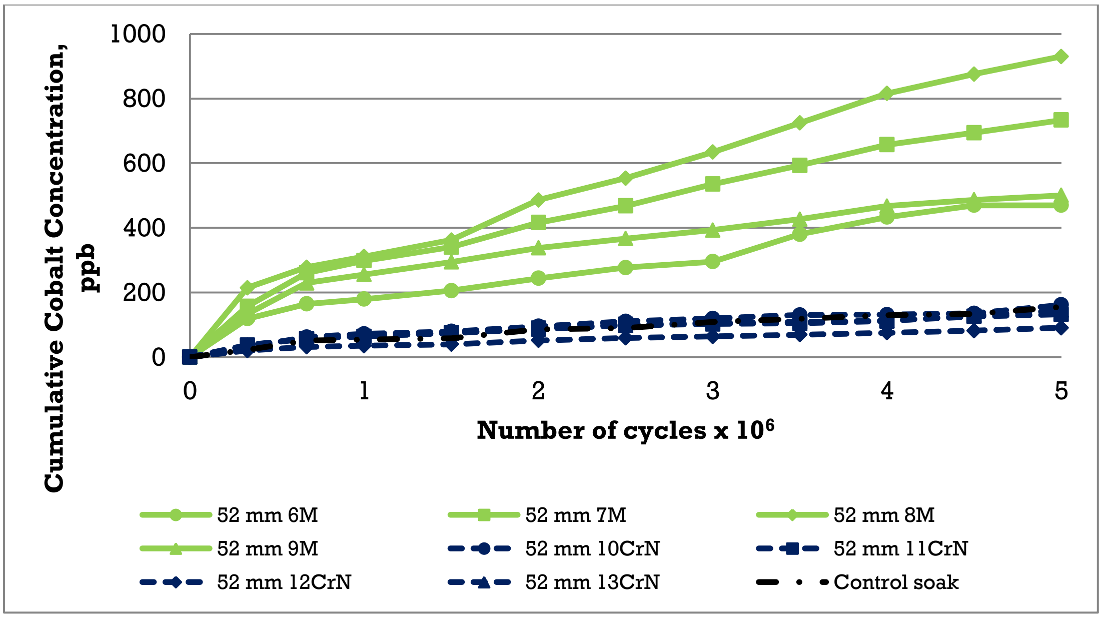


Figure 4:24: Cumulative cobalt released during five million cycles of standard testing in uncoated and CrN coated metal on polyethylene bearings

4.3.4 CrN coated and uncoated metal-on-polyethylene under adverse conditions

The introduction of alumina particles into the test fluid increased the polyethylene wear rate of the metal-on-polyethylene by 1500% in comparison to standard testing. Although one 52 mm diameter liner (52 mm 8M) was removed due to failure of the locking mechanism, runaway wear was observed in the other bearings with increased wear rates with increasing testing, Figure 4:25a. The runaway wear phenomenon observed in the metal-on-polyethylene bearings was highlighted by calculating the wear rates between gravimetric intervals with the highest rate reported between 0.67 and 1.00 million cycles, Table 4:9. One bearing wore at a higher rate than the other two, with the rise in wear occurring after 0.33 mc. When the alumina particles were removed, the uncoated metal-on-polyethylene wear rate increased further to a rate of 474.85 ± 470.35 mm^3/mc This increase was not statistically significantly increased ($p>0.05$) compared to the wear rates under standard and third body conditions, presumably due to the differing wear rates of the individual bearings during testing with the particles removed.

Table 4:9: Average polyethylene under standard, third body and further testing with the third body particles removed conditions

Bearing	Standard wear rate, mm^3/mc	Third body wear rate (0.00-1.00) mc, mm^3/mc	Third body wear rate (0.67-1.00) mc, mm^3/mc	Particles removed wear rate, mm^3/mc
52 mm MoP	10.63 ± 1.65	159.81± 108.55	368.65 ± 202.26	474.85 ± 470.35
52 mm CrNoP	9.50 ± 1.18	18.43 ± 3.17	16.35 ± 3.65	12.79 ± 3.59

The CrN coating prevented a dramatic increase in wear during the third body conditions, Figure 4:25b, but wear was significantly ($p < 0.01$) increased compared to the standard test conditions. The removal of these particles reduced the wear rate to 12.79 ± 3.59 mm^3/mc. There was no statistical significance ($p > 0.05$) between this rate and that reported in the initial standard conditions.

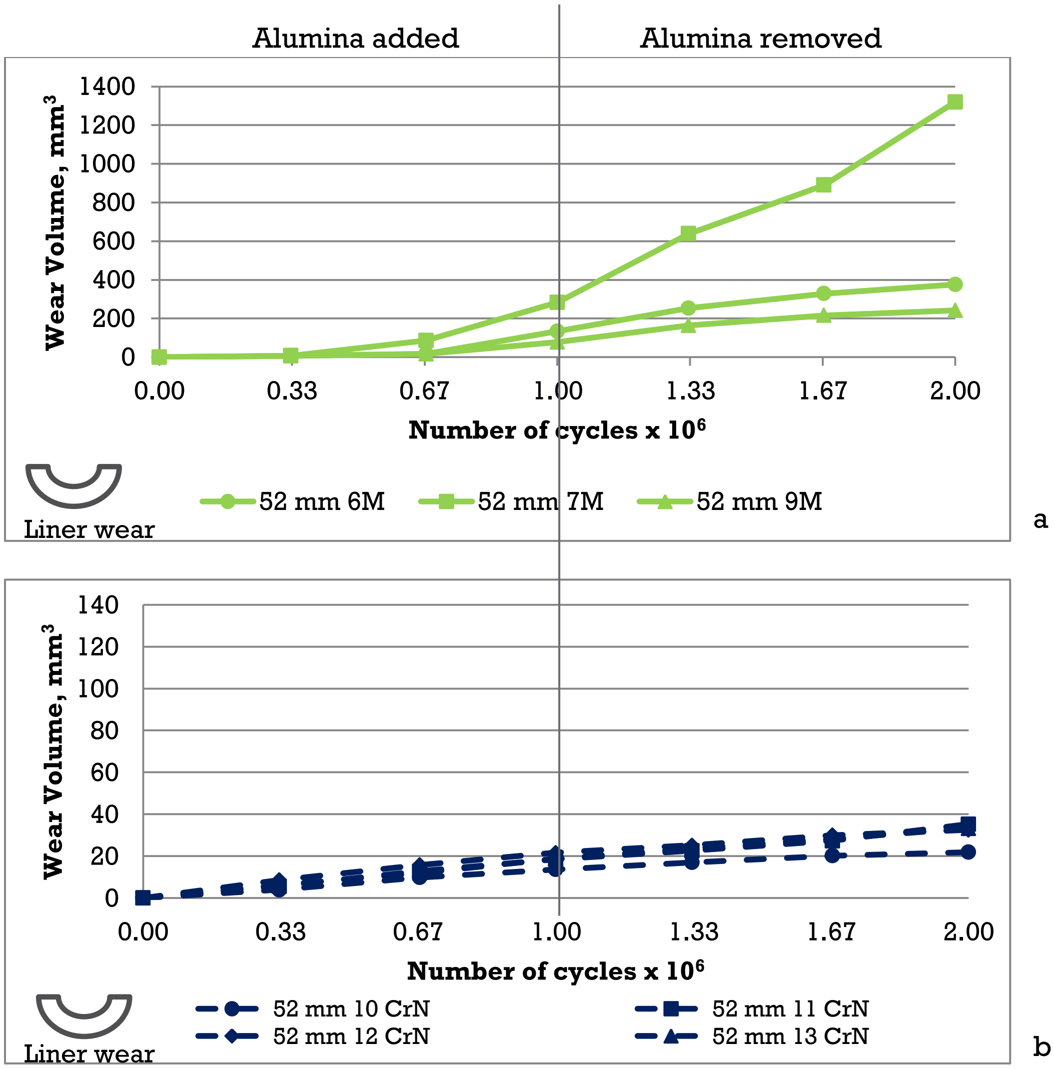


Figure 4:25: Polyethylene wear rates during testing with the addition and removal of alumina particles in the test fluid in a) metal-on-polyethylene and b) CrN coated metal-on-polyethylene bearings

The presence of the third bodies created more scratches on the metal-on-polyethylene liners, Figure 4:26. These appeared heavier than the light scratching observed under standard conditions and the highly polished wear area of these liners appeared duller. The liners paired with CrN coatings still displayed these light scratches. The surfaces of the liners did not change when the alumina particles were removed.

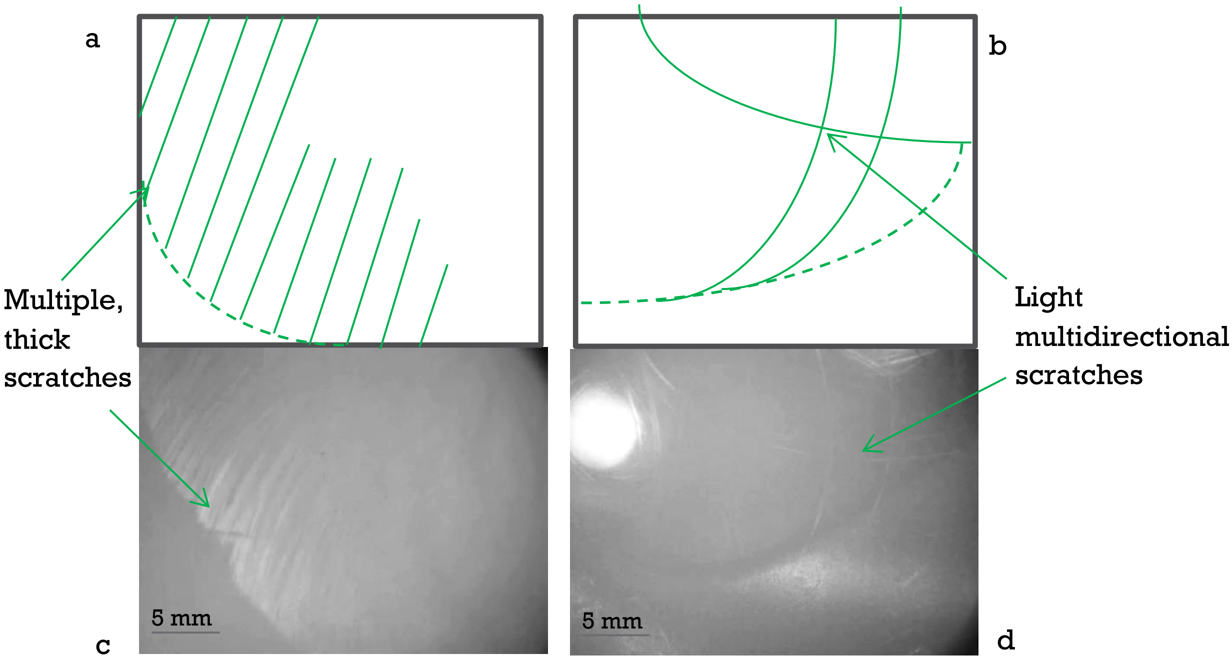


Figure 4:26: Schematic of scratching caused during alumina third body testing in (a) 52 mm diameter metal-on –polyethylene and (b) CrN coated metal-on-polyethylene and images showing (c) increased scratching in uncoated metal on polyethylene bearings while (d) the use of a CrN coating prevented this scratching

As with the liners tested with bone cement third body particles, the alumina particles embedded into the liners although this was difficult to observe as these particles were smaller than the bone cement, Figure 4:27.

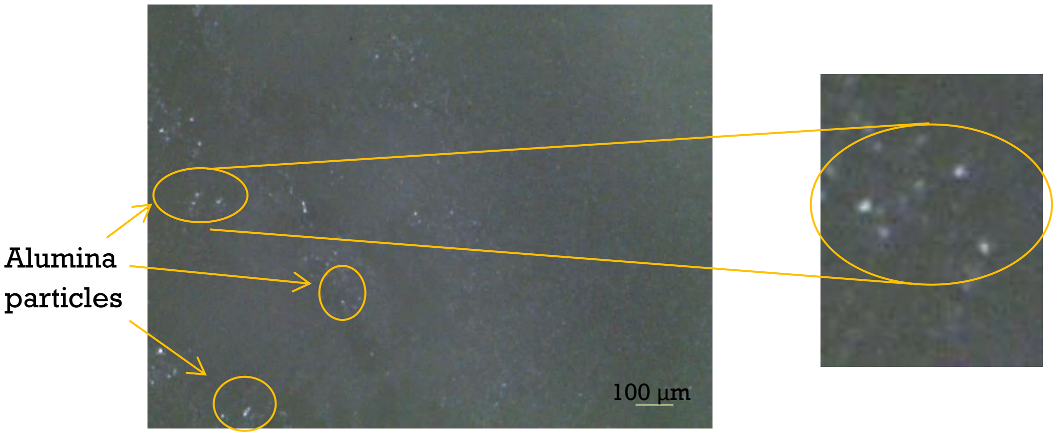


Figure 4:27: Alumina particles embedded into a polyethylene liner after 1 million cycles of third body testing

The polyethylene particles produced when paired with metal heads under third body conditions, shifted to significantly smaller particles of mode 0.05 μm, Figure 4:28. The CrN coating prevented the generation of these smaller particles, generating larger particles of mode size 0.26 μm.

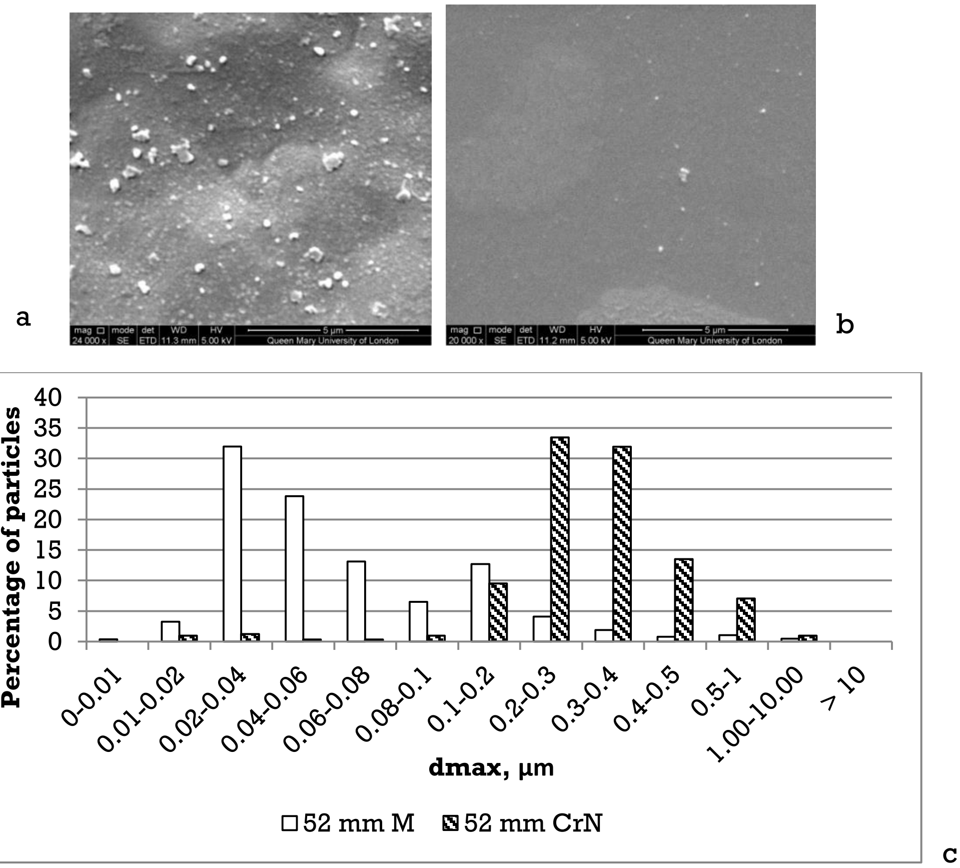


Figure 4:28: Polyethylene particles generated (a) in uncoated and (b) CrN coated metal-on-polyethylene bearings under alumina third body conditions and (c) the subsequent particle distribution

The removal of the alumina particles did not change the generation of smaller (<0.1 μm) polyethylene particles observed under third body conditions in the metal-on-polyethylene bearings with a mode of 0.07 μm, suggesting that this was caused by the damage on the heads, Figure 4:29. There particles were larger than those produced under third body conditions, presumably due to the generation of more elongated particles, Figure 4:30, which would increase the maximum diameter measured.

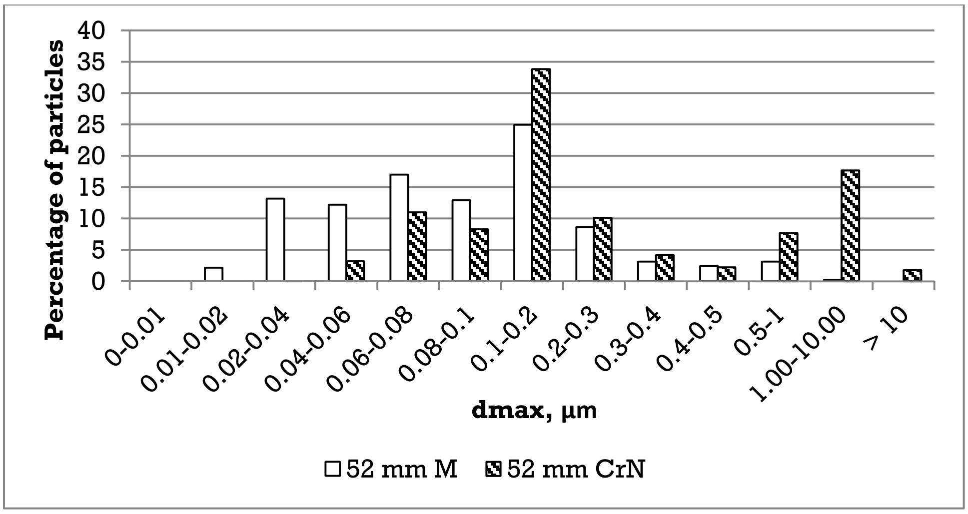


Figure 4:29: Polyethylene particle distributions after testing with the removal of third body particles

In the coated bearings, the particle distributions maintained the majority of particles sized between 0.1-0.2 µm as observed in the original standard test conditions. However, more particles sized between 1 and 10 µm were generated with the removal of third body particles from the test fluid.

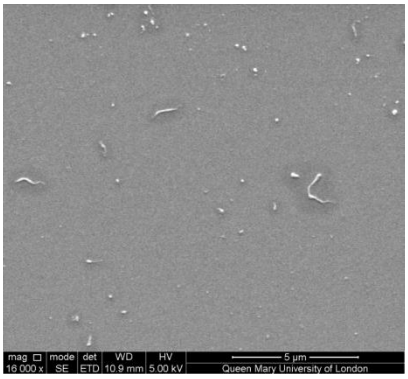


Figure 4:30: Scanning electron microscopy image of polyethylene particles showing the generation of elongated particles as well as spherical particles

Increased wear was observed in both types of heads during third body testing suggesting the alumina particles removed material from these surfaces, Figure 4:31. In the uncoated heads, wear rates of 9.92 ± 5.39 mm^3/mc were produced signifying significant material removal. The highest head wear rate in the bearing (between 0.67 and 1 million cycles) was significantly ($p<0.01$) greater than the standard run-in wear rate. There was no difference ($p>0.05$) between the wear rate of the CrN coating between 0.67 and 1 million cycles under third body conditions (1.13 ± 0.22 mm^3/mc) compared to the standard run-in wear rate although some wear may have been the removal of the proteins which adhered during standard testing.

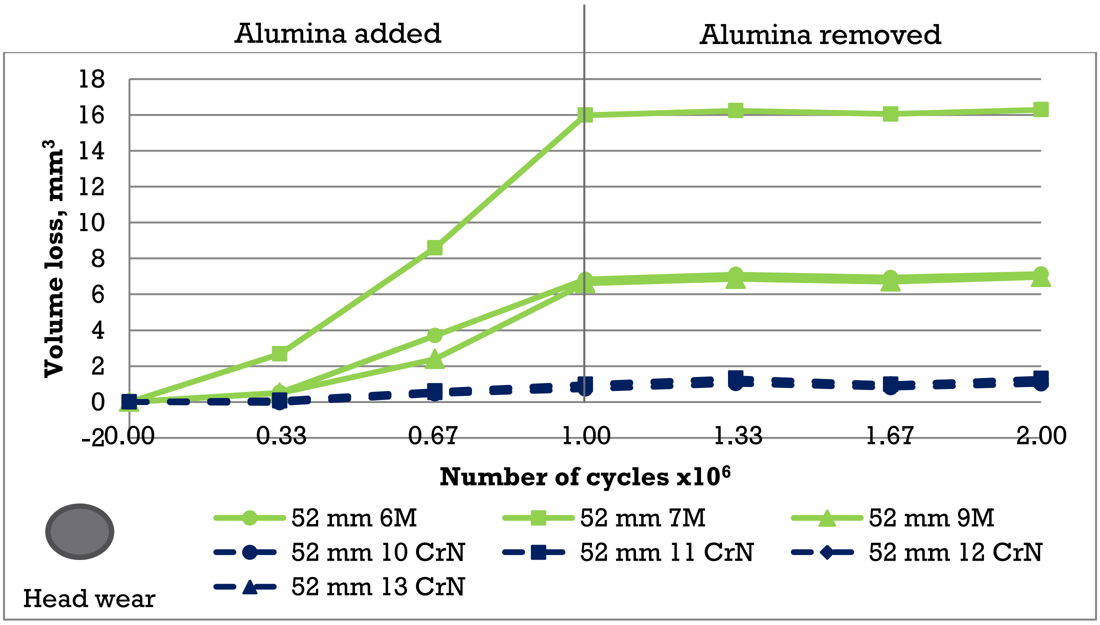


Figure 4:31: Head volume loss in uncoated and CrN coated heads during the addition of alumina third body particles and after the removal of these particles from the test fluid

The wear in both sets of heads reduced with the removal of the alumina particles compared to third body conditions. The wear patterns were similar throughout the 1 million cycles with gain reported between 0.33 and 0.67 million cycles of this testing. In these heads, as in the first million cycles of standard testing, no difference was observed between the coated and uncoated heads.

After 1 million cycles of testing with the alumina third body particles, the uncoated heads showed pits dragged directionally created by the alumina particles, Figure 4:32a. This did not change the Ra of the heads but did increase the Rz and Rt showing a change in surface profile with large valleys and peaks, Table 4:10. The CrN heads did not show this damage with the surface profile only showing variation at a nanometre scale, Figure 4:32b. This maintained a low Ra, Rz snd Rt in the coated heads.

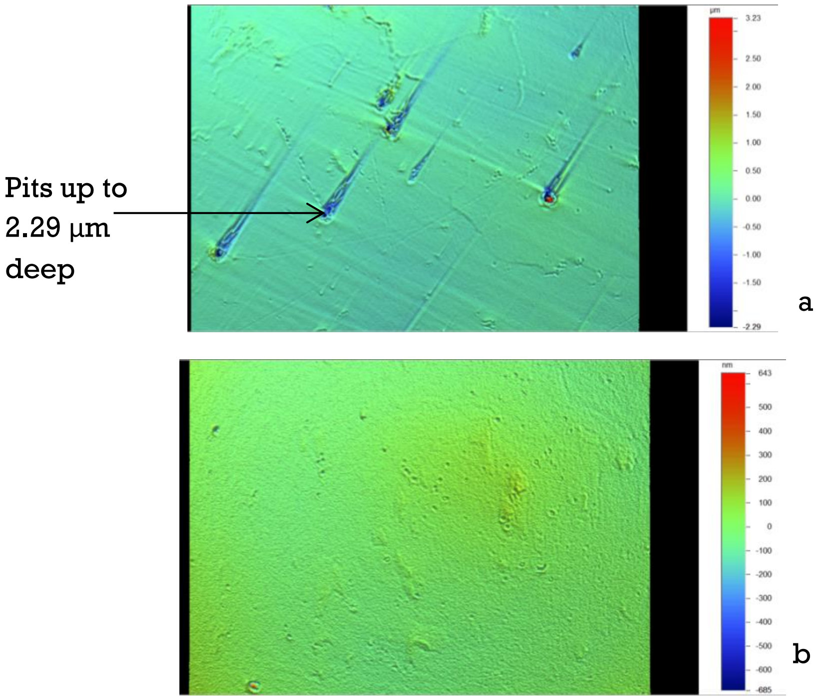


Figure 4:32: Optical surface profilometry image of (a) 52 mm uncoated and (b) CrN coated metal head after third body testing with alumina particles

Table 4:10: Average surface roughness of the heads after one million cycles of third body testing showing increased roughness in the uncoated heads

Head	**Ra, µm (± 1 sd)**	**Rz, µm (± 1 sd)**	**Rt, µm (± 1 sd)**
52 mm uncoated metal	0.018 (± 0.010)	2.730 (± 1.127)	4.756 (± 1.762)
52 mm CrN coated	0.007 (± 0.003)	0.820 (± 0.348)	1.933 (± 0.936)

As well as the increased roughness and formation of pits in the uncoated heads, alumina particles were observed on the heads, Figure 4:33. These appeared at the end of the scratches instead of the pits on the heads suggesting that in some instances the alumina particles remained on the heads. These were not observed in the coated heads possibly because the coating was harder than the uncoated metal preventing the alumina from embedding on the surface.

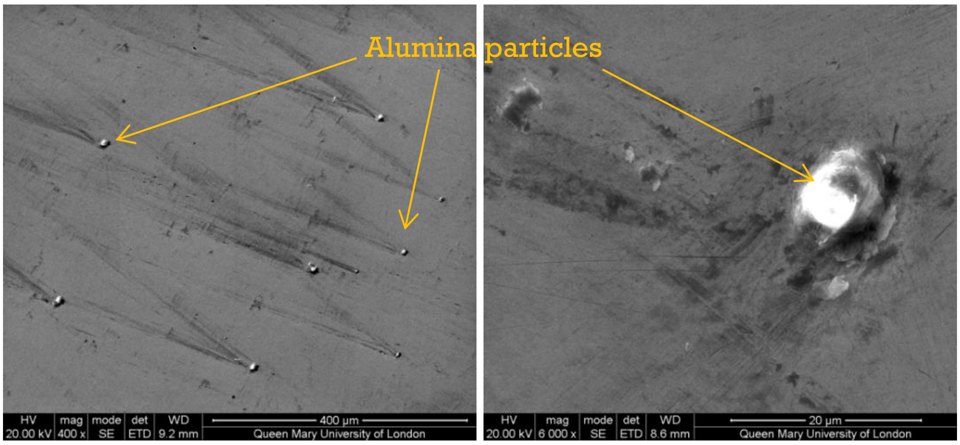


Figure 4:33: Scanning electron microscopy images of uncoated metal heads after 1 million cycles of third body testing showing alumina particles embedded on the surface

Cobalt release measured throughout alumina third body testing was negligible in the CrN coating but was pronounced in the uncoated bearings. The amount of cobalt was substantial, up to 4,400 ppb, within the first 86,400 cycles in the uncoated metal-on-polyethylene bearings, Figure 4:34. This was over 6 times higher than the total cobalt released over 5 million cycles of standard testing.

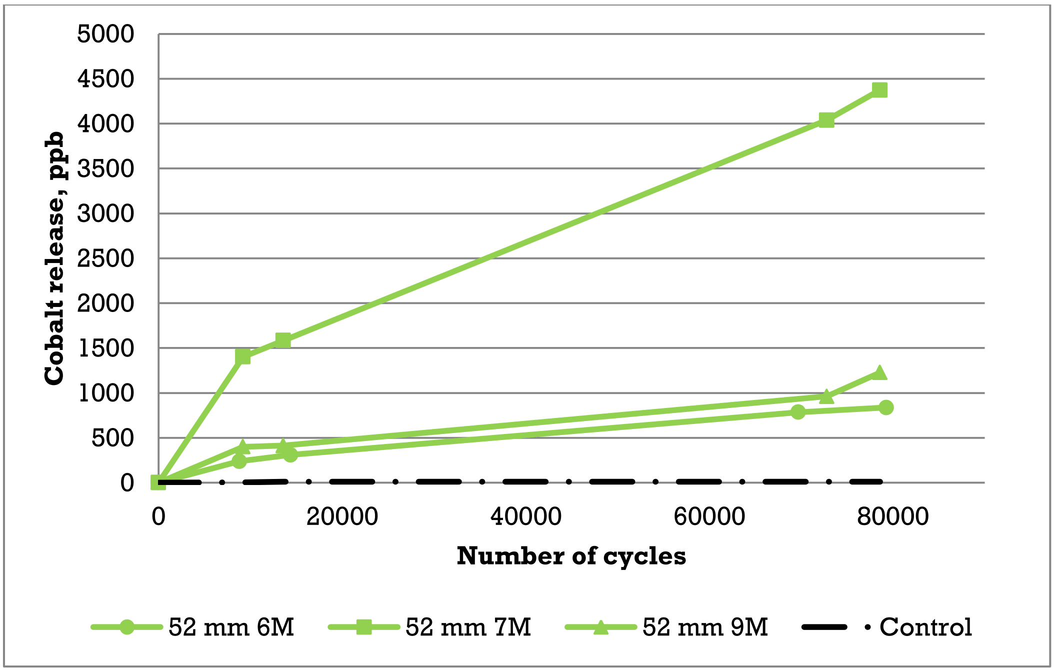


Figure 4:34: Cobalt released in metal-on-polyethylene bearings within the first 24 hours (86,400 cycles) of testing with alumina particles

After one million cycles of third body testing, the mean amount of cobalt released into the test fluid from the metal-on-polyethylene bearings tested with alumina particles was 70,700 ± 32,500 ppb, Figure 4:35, signalling significant removal of material from the heads. The cobalt released in the metal-on-polyethylene bearings over this time was found to correlate linearly with head wear (Pearson's correlation of 0.97). No measurable cobalt was found in the test fluid of the CrN coated heads after one million cycles of testing.

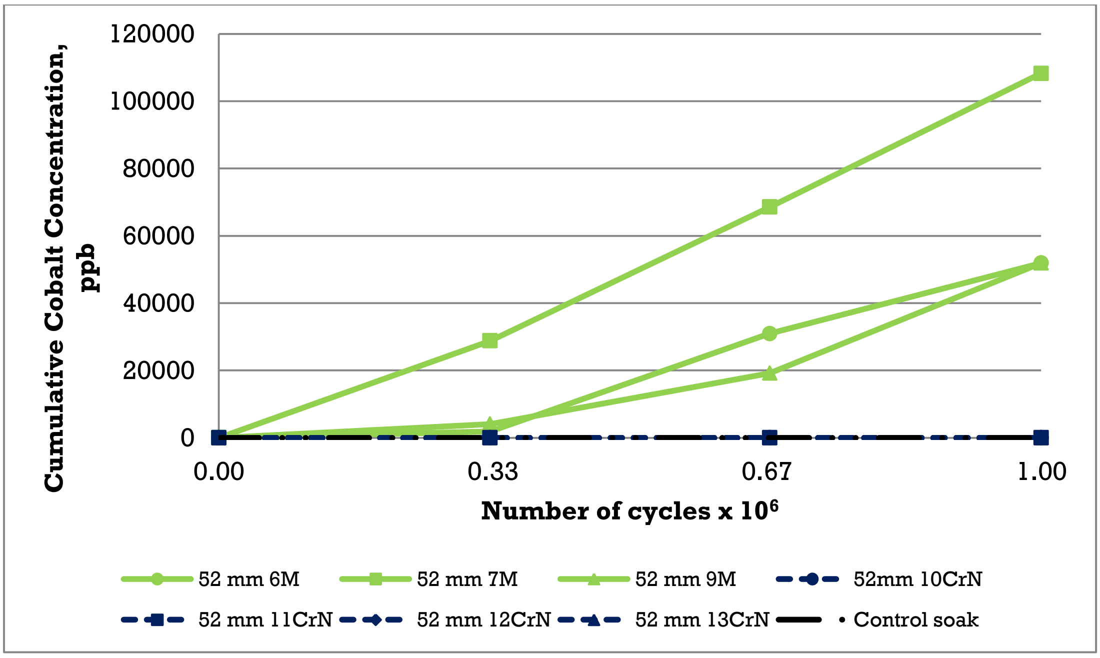
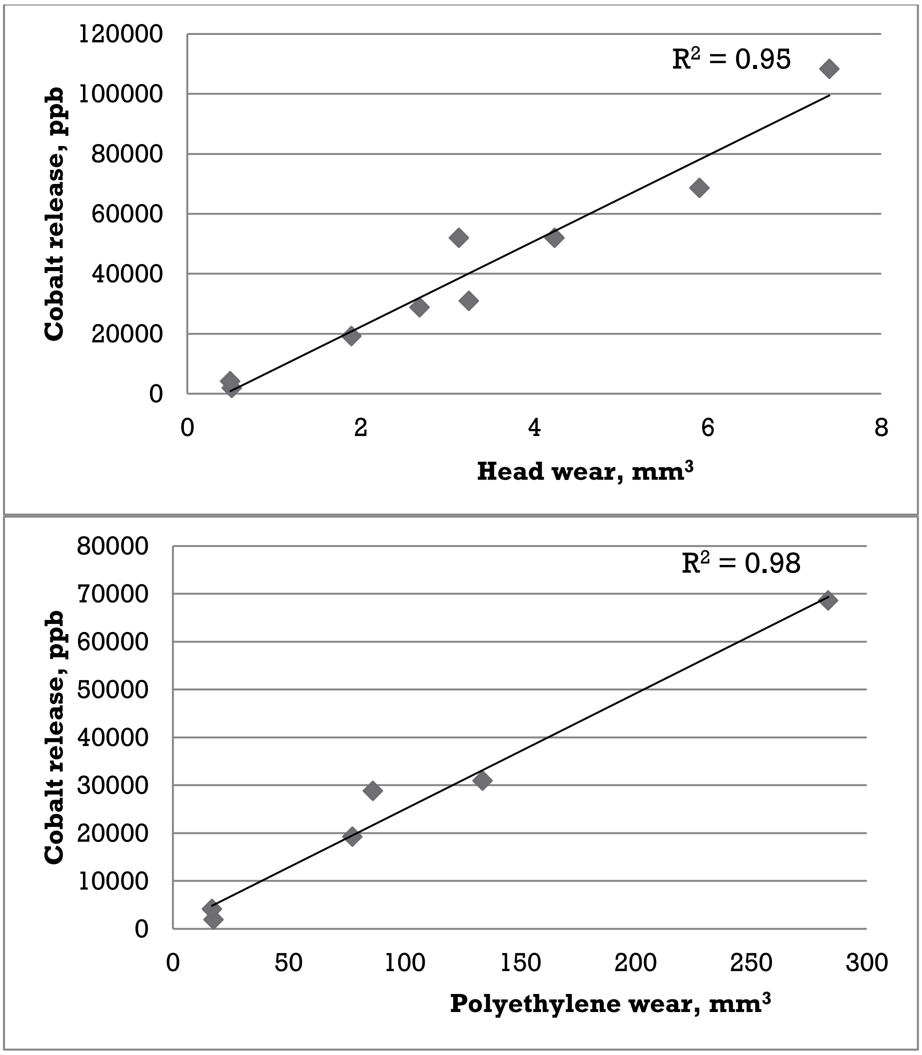


Figure 4:35: Cumulative cobalt released over one million cycles of testing with alumina third body particles

Cobalt release measured in the metal-on-polyethylene bearings during this testing also related to polyethylene wear, with cobalt levels indicating the subsequent polyethylene wear (at the next gravimetric interval) in the metal-on-polyethylene bearings with a Pearson's correlation of 0.99, Figure 4:36. As the cobalt release and head wear was also related, this led to similar relationships between the head wear and polyethylene wear highlighting that polyethylene wear is dependent of the damage to the head.

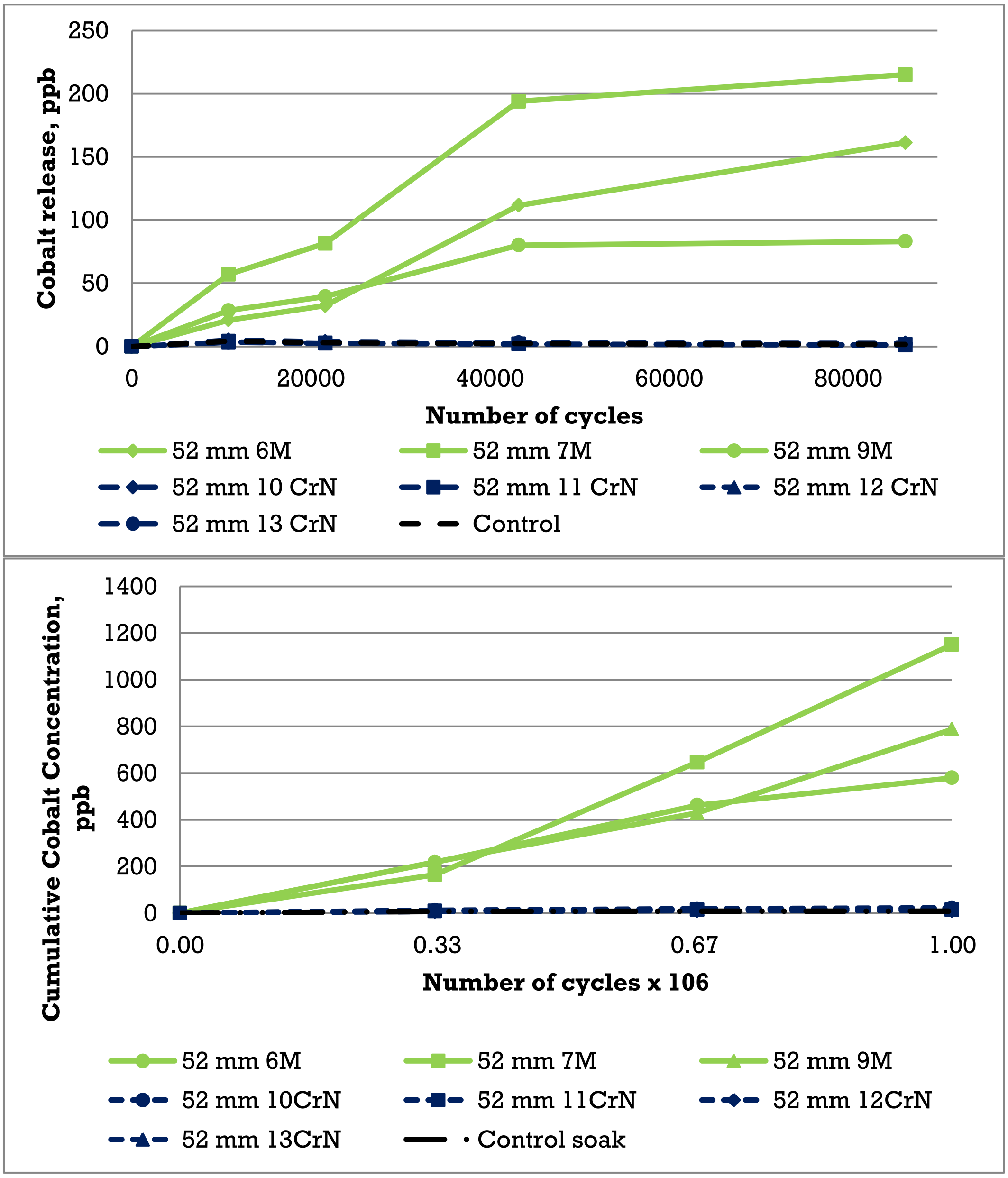


a

b

Figure 4:36: Liner relationship between cobalt release and (a) head wear at the same time point and (b) subsequent polyethylene wear in metal-on-polyethylene bearings tested with alumina third body particles

Cobalt release was measurable in all uncoated heads during testing with the third body particles removed, showing a steady increase in cobalt as testing progressed. Over the first 24 hours, cobalt release was reduced from that observed in the first 24 hours of standard testing, Figure 4:37a. Over the full 1 million cycles however, the roughened uncoated heads increased in cobalt release ($p<0.01$) in comparison to that observed in standard (pristine) conditions, Figure 4:37b. This could be due to the embedded alumina particles in the polyethylene liners, increasing the amount of material removed from the uncoated heads. The CrN coating remained effective at preventing any cobalt release, releasing only 16.52 ± 5.28 ppb suggesting that this remained fully adhered even with further abrasion.



a

b

Figure 4:37: Cobalt release a) within the first 24 hours (86,400 cycles) and b) over 1 million cycles of testing after the removal of third body particles showing negligible cobalt from the coated components

Simulated jogging with the uncoated alumina damaged heads was found to result in little increase in the polyethylene wear rates of the bearings compared to the previous walking test, Figure 4:38. The polyethylene liners observed after jogging testing showed the same scratching as had been observed in the walking test suggesting that the short durations of simulated jogging had not adversely influenced the wear behaviour.

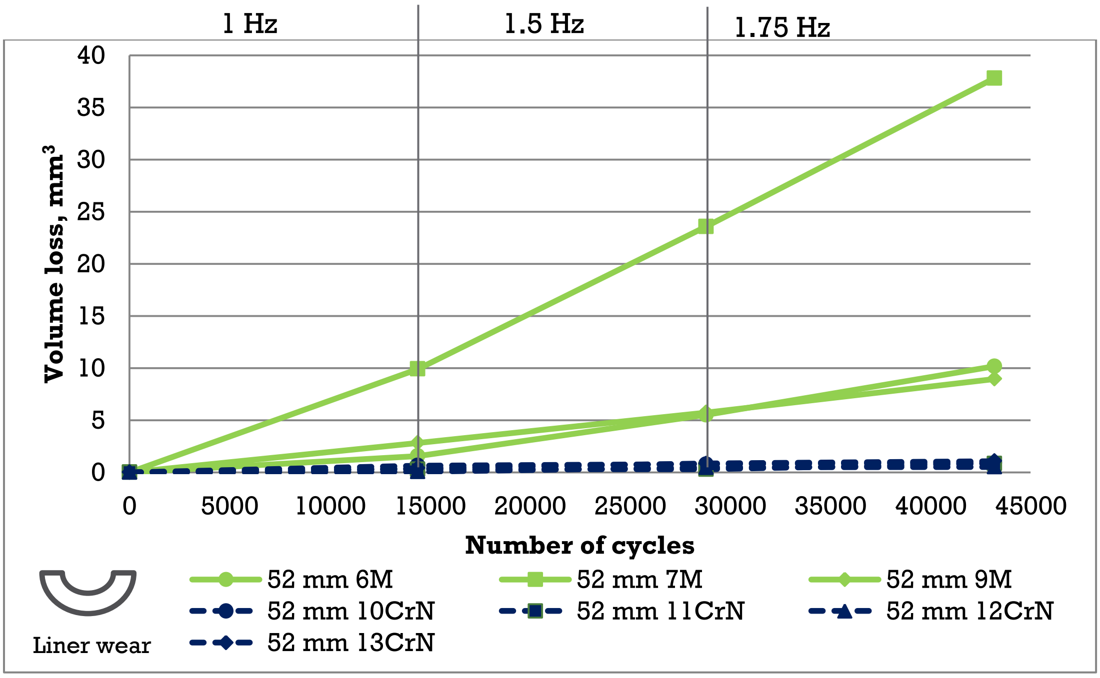


Figure 4:38: Polyethylene wear of 52 mm metal and CrN on polyethylene under simulated jogging at three different speeds

There appeared to be little influence of speed on the CrNoP bearings with wear rates decreasing with increasing speed, although this was not significant ($p>0.05$), Table 4:11. While the wear rate did increase with speed in the MoP bearings, this was also not significant as there was variability in the wear rates of these bearings.

Table 4:11: Mean polyethylene wear rate (± 1 standard deviation) after jogging at different speeds

	1Hz jogging wear rate, mm^3/mc	**1.5 Hz jogging wear rate, mm^3/mc**	**1.75 Hz jogging wear rate, mm^3/mc**
52 mm metal on polyethylene	330.5 ± 312.6	475.5 ± 412.2	512.2 ± 514.8
52 mm CrN on polyethylene	23.6 ± 16.8	17.9 ± 14.7	16.3 ± 15.2

The particles produced under jogging conditions in the uncoated metal-on-polyethylene continued to display larger quantities of particles less than 0.1 μm than standard walking, Figure 4:39a. Under the slow jogging conditions, approximately 15 % of particles were larger than 0.5 μm with a trend showing smaller particles generated as jogging speed increased. Conversely, the polyethylene particles generated from articulating against the CrN coated heads, appeared to increase in size with increasing jogging speed. In all cases, the majority of particles were sized between 0.1 and 0.2 μm with increasing numbers of particles generated larger than this, Figure 4:39b.

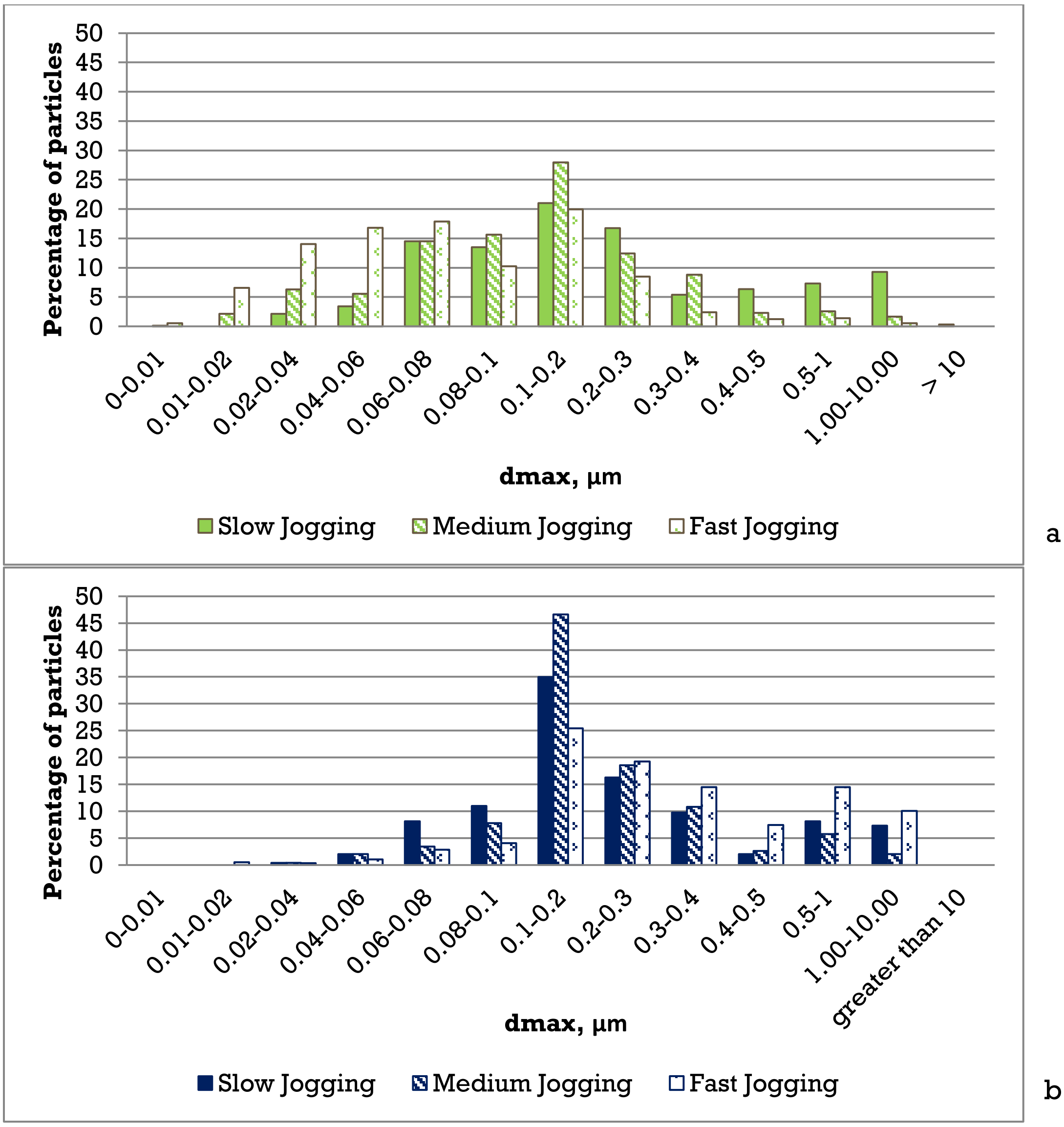


Figure 4:39: Particle distribution a) for metal on polyethylene and b) CrN coated metal on polyethylene bearings under slow (1Hz), medium (1.5 Hz) and fast (1.75 Hz) jogging conditions

Due to the short duration of the tests, no head volume loss was observed. Cobalt release, however, was still measureable in the test fluid in the MoP bearings, Figure 4:40. The bearings with the CrN coating produced slightly more cobalt than the soak control but this was not significant.

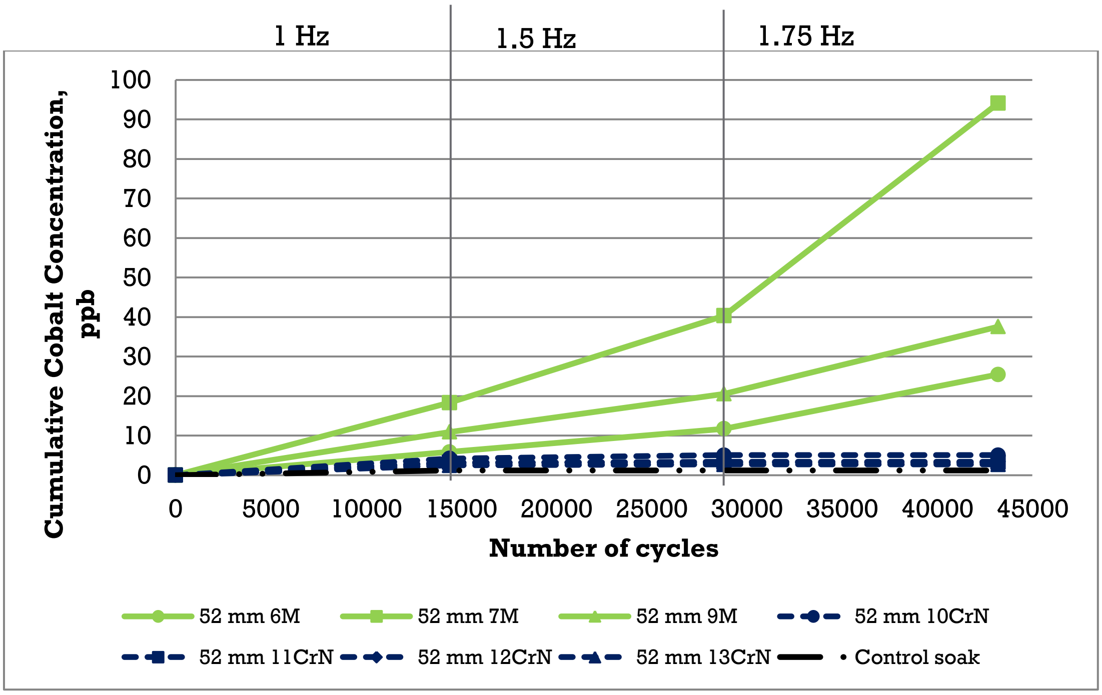


Figure 4:40: Cobalt release during simulated jogging conditions

No correlation was established between head wear and cobalt release but cobalt release linearly correlated to polyethylene wear produced at the same speed, Figure 4:41. This showed slight increases in both polyethylene wear and cobalt release observed with increasing speed of simulated jogging.

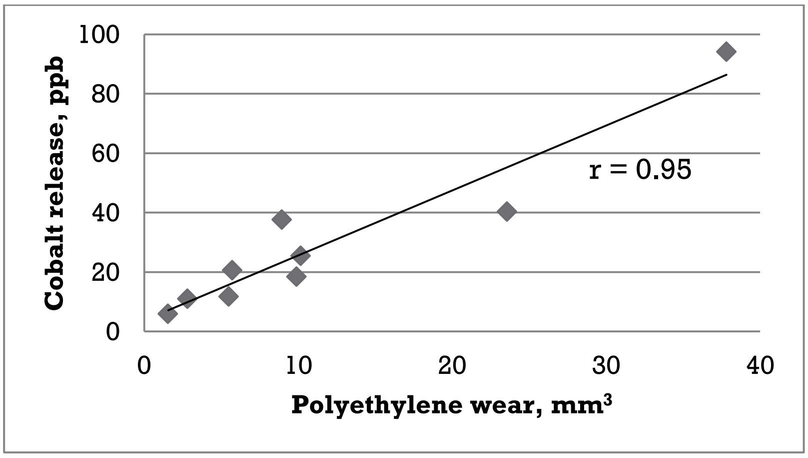


Figure 4:41: Linear relationship between polyethylene wear and cobalt release under simulated jogging

The Ra of both heads increased following jogging but this change was not significant ($p>0.05$), Table 4:12. Changes in the Rz values, however, were significant ($p<0.01$) with the uncoated heads becoming smoother and the CrN coated heads becoming rougher although this was still smoother than the uncoated heads.

Table 4:12: Mean surface roughness of heads before and after simulated jogging showing little difference in roughness parameters

Head	Ra , µm		Rz , µm	
	Before jogging	**After jogging**	**Before jogging**	**After jogging**
Metal	0.019 ± 0.011	0.027 ± 0.014	3.012 ± 1.613	2.724 ±1.212
CrN	0.006 ± 0.002	0.008 ± 0.003	0.660 ± 0.479	0.845 ± 0.642

4.4 Discussion

4.4.1 The effect of soaking

Determining polyethylene wear gravimetrically can be problematic due to polyethylene's ability to absorb water over time. All soaking in this current study was performed in deionised water, although soaking in bovine serum has also been reported (Brandt et al., 2011). Two main differences exist between these fluids; the ion concentration and the presence of proteins. Although it has been shown that serum leads to greater increases in mass during soaking, when soaked in buffered phosphate solution (i.e. ions but no proteins) this increase was not observed (Brandt et al., 2011) indicating that this higher mass gain is due to the proteins. Protein absorption or binding to the polyethylene has been observed in some retrievals (Wooley et al., 1999). Therefore, the amount of fluid absorbed may be the same as when soaked in water but the proteins adhered to the surface of the polyethylene may result in a greater mass gain. This may also explain why the difference in mass gain when soaked in water and bovine serum is more noticeable at 37°C than at room temperature (Brandt et al., 2011). The effect of soaking medium on the subsequent wear rate has not been reported in the literature.

Little difference has been reported in the soak characteristics of non-crosslinked and moderately (50 kGy) crosslinked polyethylene under the same soak conditions (Liao and Hanes, 2006). In the pre-soaking of the test components in the current study it was observed that 28 mm highly crosslinked polyethylene liners containing vitamin-E absorbed less water than a moderately crosslinked liner not containing vitamin-E. After 84 days in soak, the vitamin-E blended liners absorbed 3.5 mg (0.11 % gain in mass) in comparison to 5.0 mg over 73 days in the liner not containing vitamin-E (0.20 % gain). The vitamin-E liners achieved fluid absorption stability after 50 days while the moderately crosslinked liner did not, suggesting the inclusion of vitamin-E may alter the soak behaviour of the polyethylene. Nusbaum and Rose (1979) have suggested that the presence of free radicals in polyethylene after sterilisation increase the carbonyl groups in the material and therefore make it more hydrophilic. The inclusion of vitamin-E to prevent the generation of these free radicals would therefore reduce this hydrophilic property and consequently result in less water uptake, as observed in the current study. Other differences between the materials which originated from different manufacturers may also have influenced the soak behaviour of the material. The standard crosslinked liner was shaped from bars of GUR1050 while the vitamin-E liners were made from pucks of GUR1020 which possesses a lower molecular weight than the GUR 1050.

The soak behaviour between the vitamin-E blended liners was also different. The short soak 52 mm diameter liners absorbed water at an initial rapid rate and then reached stability at 20 days, The long soak 52 mm diameter and 28 mm diameter liners appeared to absorb water more slowly and therefore it took longer to reach stability. In the 52 mm diameter liners, this was approximately 30 days (1.5 times longer than the short soak liners) while the 28 mm diameter liners only reached stability after 50 days (2.5 times longer). Despite this, all liners showed stability at approximately 0.1 % mass gain. The increased soak duration required in the 28 mm diameter bearings was possibly attributed to the increased thickness of these liners. All liners had the same external diameter yet the 28 mm diameter were 7 -8 mm thicker than the 52 mm diameter liners, meaning the diffusion distance would be greater for the smaller liners. Tibial polyethylene implants soaked in water have shown increased fluid absorption (0.5 mg) with an increased thickness of 4 mm was but this was not statistically significant (Brandt et al., 2011).

Within the two sets of 52 mm diameter vitamin-E blended polyethylene liners soak duration was altered with one set soaked for 53 days and the other for 606 days. This difference in 553 days ultimately resulted in double the fluid uptake in the long term soak liners and correlated with a 65% increase in wear rate. Studies considering the duration of soak time from 46 and 92 days have observed no difference in mass gain due to fluid absorption (Brandt et al., 2011). The difference in soak duration in the current study was much greater. It has been reported (Brandt et al., 2011), that disturbances in fluid soak to clean and weigh polyethylene resulted in an increase in water absorption from 1.69 mg to 2.78 mg. Although both sets of liners in the current study were initially disturbed to equal amounts, the long soak liners were left for 432 days undisturbed following this and gained 1.02 mg over this period (0.002 mg/day). In contrast, the final 95 days of soaking resulted in 0.66 mg fluid gain (a rate of 0.007 mg/day) suggesting that this disturbance of the liners may have increased their fluid gain further, Figure 4:42.

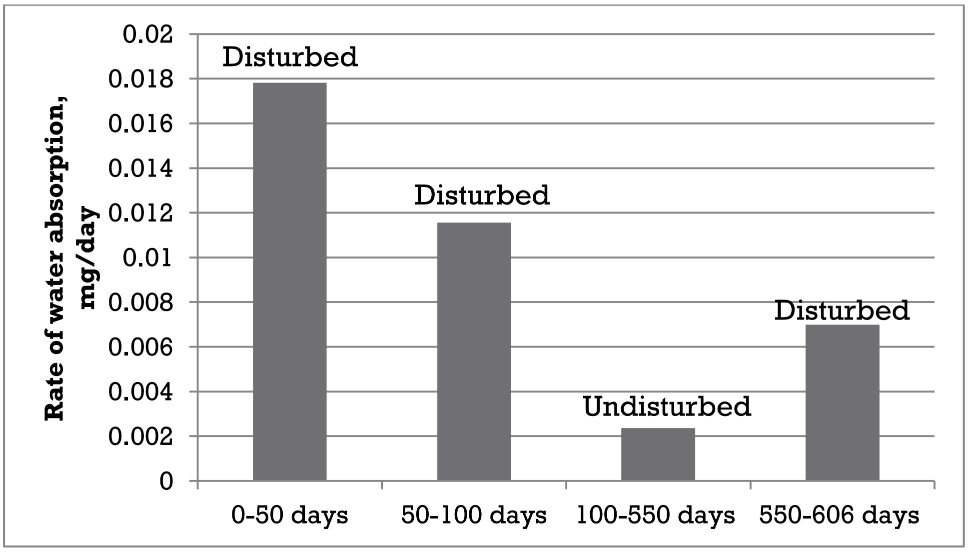


Figure 4:42: Rate of water absorption in the long soak 52 mm liners showing increased rate of absorption during the first 100 days and final 56 days of soaking, when the liners were frequently disturbed to measure fluid uptake

The increased hydration levels of the long soak polyethylene is the probable cause for the increase in wear observed under standard conditions compared to the short soak liners. Yao et al., (2003) observed initial increases in pin-on-disk wear rates in polyethylene with higher hydration. In their study, a difference of 0.74 mg water absorption between highly hydrated and non-hydrated polyethylene pins produced a significant, 26% increase in the wear rate of the hydrated pins. This study used a simplistic wear model with constant loading, yet observed that the influence of increased hydration decreased over time with no significant difference observed between wear rates at 1 million cycles. Liao and Hanes (2006) also considered the influence of hydration on polyethylene wear rates but in a hip simulator; a run-in period was observed in the highly hydrated liners due to an increased fluid release due to loading. The use of a loaded soak control to correct the wear rate for this loss of water showed wear rates comparable to moderately hydrated bearings. Increased fluid loss has been observed in loaded soak controls in comparison to motion only soak controls (Estok et al., 2007) suggesting that loading expels water absorbed in polyethylene and this mass loss would be measured as wear if not corrected with a loaded soak control. The current study did not utilise a loaded soak control which may have resulted in the increased wear rate reported in the long term soak bearings. In all 52 mm diameter liners soaked for different durations, the wear reported in mg divided by the total water mass gain measured before testing was far more consistent than the wear reported alone, Figure 4:43. In the first third of a million cycles, this ratio varied from 1.55 to 2.57 apart from one bearing (8M) which ultimately failed due to excessive wear of the locking mechanism suggesting wear at this interface may have occurred throughout testing. The consistent initial ratio may be explained as a water absorption effect. Liao and Hanes (2006) reported an increased run-in wear rate in highly hydrated bearings over only the first half of a million cycles only suggesting the initial wear rate may be due to fluid explusion. As testing continued to 1 million cycles, a small difference was observed with the long soak liners displaying a smaller wear to absorption gain ratio suggesting the relationship between fluid absorption and wear is not as strong in the less hydrated bearings. As the inclusion of vitamin-E into polyethylene may alter the absorption behaviour, it is possible that this also alters the release of the water in these bearings leading to a lower rate of water release in highly hydrated bearings and produced a prolonged, elevated wear rate. The wear rate of the long soak polyethylene bearings was significantly lower at 13.33 ±1.61 mm^3/mc in the final million cycles of testing which further validates this reasoning.

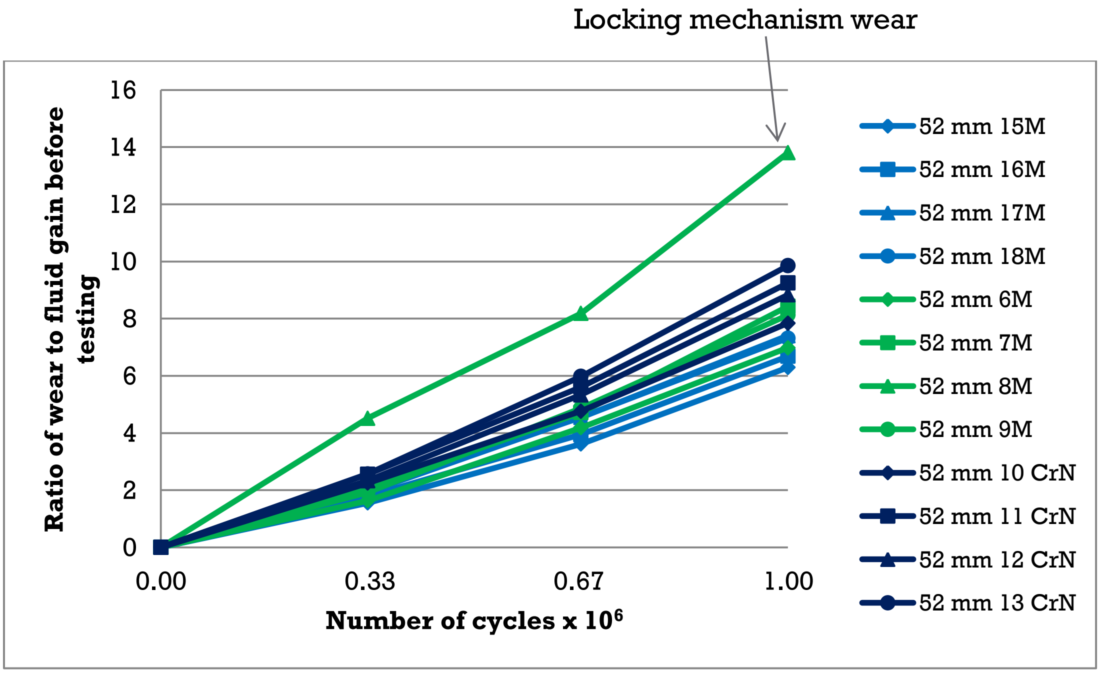


Figure 4:43: Reported polyethylene wear in mg divided by mass gain reported during pre-soaking in all 52 mm diameter polyethylene liners displaying a relationship between soaking and wear

4.4.2 Influence of diameter and the potential for large diameter metal-on-polyethylene bearings

Bearing diameter in metal-on-conventional polyethylene bearings has been limited due to the wear volume produced (Charnley et al., 1969). Theoretically, following Archand's wear law as described in equation 4, section 2.1.3, a larger diameter should increase both the contact area and sliding distance thereby increasing the wear rate (Affatato, 2012). This has been widely confirmed , with a 4-10% increase in wear with increasing diameter from 28 mm to 36 mm in metal-on-polyethylene bearings (Shen et al., 2011) and a 5-9% increasing diameter from 22 mm to 28 mm in alumina-on-polyethylene bearings (Clarke et al., 1996).

Larger differences have been seen comparing 28 mm diameter metal-on-polyethylene bearings to 46 mm diameter bearings with wear rates of 14 and 51 mm^3/mc respectively (Muratoglu et al., 2001).

The introduction of crosslinking to reduce polyethylene wear has made it more challenging to distinguish the influence of diameter on wear. Increasing wear has been reported in alumina-on-90 kGy irradiated polyethylene with wear rates of 10.8 and 16.7 mm^3/mc reported in the 36 and 44 mm diameter bearings yet wear in the small, 28 mm diameter bearings was negligible (Zietz et al., 2013). Muratoglu et al., (2001) reported no measurable wear in polyethylene crosslinked at 95 kGy at diameters of 22, 28, 38 and 46 mm thus making it difficult to establish a relationship between wear and diameter. The wear of sequentially crosslinked polyethylene, however, has reported wear in 32-52 mm diameters but shown poor correlation with head size (Herrera et al., 2007).

Due to the low wear of crosslinked polyethylene, the use of larger diameter vitamin-E highly crosslinked polyethylene bearings have been proposed (Oral et al., 2012) but no studies have previously considered the influence of diameter in vitamin-E blended highly crosslinked bearings. The current study has shown that an increase in diameter from 28 mm to 52 mm significantly increased wear by 31%. The bearing sizes tested represent the extremes of diameter size and showed a difference in wear rate of 2.3 mm^3/mc. In a study by Herrera et al., (2007), the increase in wear rate between two extremes of diameter was more pronounced than the current study with 1.4 ± 0.7 mm^3/mc in 32 mm diameters and 4.8 ± 3.1 mm^3/mc in 52 mm diameters. The lower wear rate than that observed in other 52 mm diameter bearings may be explained by the highly polished surface finish (Ra 0.004 ± 0.001 μm) achieved on the heads (Herrera et al., 2007). Although the wear rate of the 52 mm diameter bearings in the current study was greater than the reported wear in the Herrera et al., (2007) study; the wear rates reported in the both diameters of the current study were similar or lower than the literature overall, Figure 4:44. The polyethylene wear rate of the 52 mm diameter bearings was comparable to 36 mm diameter bearings crosslinked at 95 kGy (Galvin et al., 2010) and 36 mm diameter hindered phenol anti-oxidant stabilised polyethylene irradiated at 115 kGy (Partidge et al., 2013). The 28 mm diameter bearings in the current study, produced wear rates comparable to the 5 ± 2 mm^3/mc of 28 mm diameter metal-on-100 kGy crosslinked polyethylene (Fisher et al., 2006) and the 6.1 mm^3/mc in 28 mm diameter 0.1 wt% vitamin-E blended polyethylene crosslinked at 100 kGy (Lerf et al., 2013). In bearings of the same material as that tested in the current study, wear rates of 1.81 mm^3/mc have been reported at a diameter for 40 mm (Traynor et al., 2011) highlighting the potential for differences in wear between laboratory studies even when following ISO standard conditions.

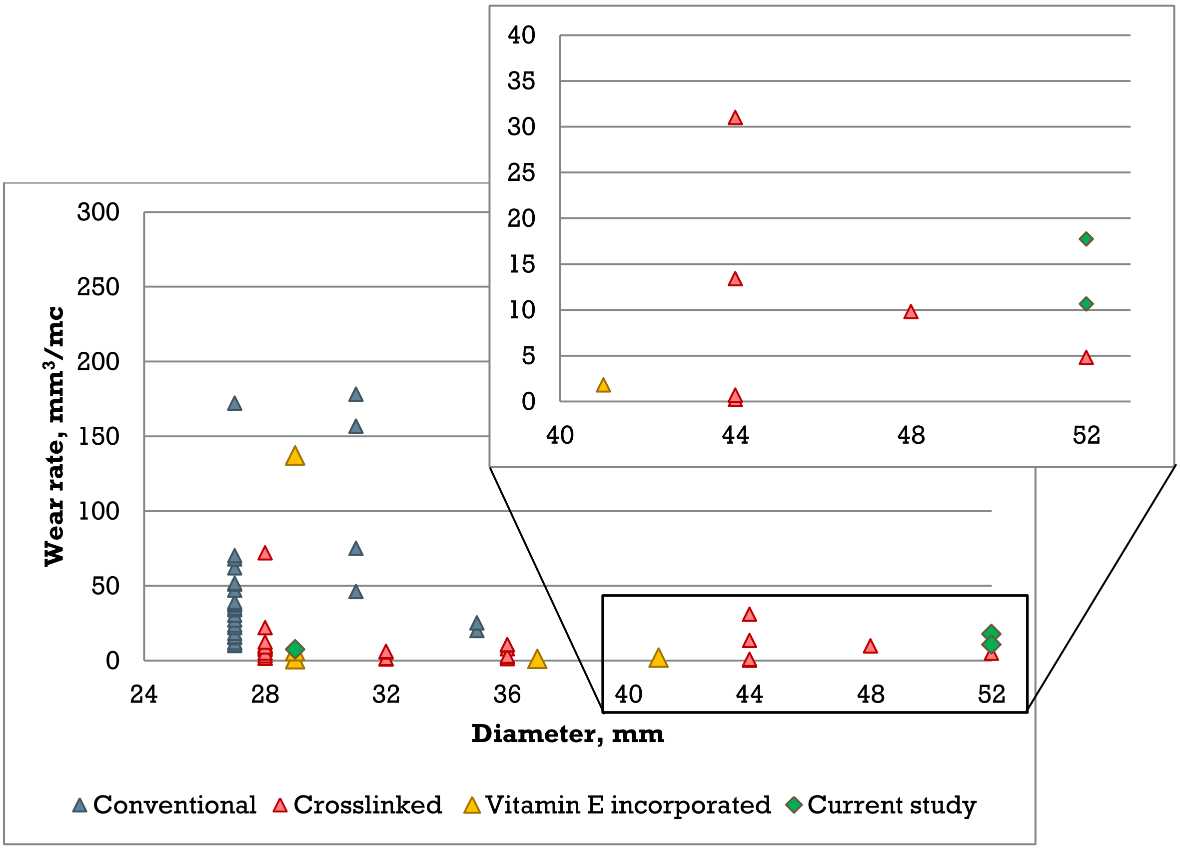


Figure 4:44: Graph showing wear rates reported in the current study comparable to that reported in the literature for standard test conditions

Differences in design can also lead to differences in wear rates. Significant differences between the two bearing diameters tested in the current study have been acknowledged, Table 4:13, which may have confounded results. Liner thickness is believed to influence the stresses within polyethylene with thinner liners increasing the wear rate and leading to an increased risk of fracture (Oonishi et al., 1998). In a hip simulator study considering only liner thickness, however, a decrease of 3 mm in thickness resulted in a decrease of wear by 19% (Shen et al., 2011), attributed to decreasing contact area despite increased contact stresses. In contrast, an increase of 4 mm in the thickness of 32 mm diameter, 90 kGy irradiated polyethylene liners have been shown to lead to insignificant increases in wear (Herrera et al., 2007). The liner thickness in the current study varied by 8.4 mm in the loaded areas which represents a much larger difference in thickness than previous studies and therefore may have produced a greater difference in wear than if comparable thicknesses were used. Other differences in the design of the liners, for example different locking mechanisms to prevent rotation may have also affected wear rates with different stress distributions in the material. Different locking mechanisms have been shown to alter micromotion and backside wear of the liners (Williams et al., 1997). Wear of the locking rosette of one of the large diameter bearings of the current study was observed and therefore undetected wear of this feature in the other bearings may have also occurred. This would increase the wear rate reported, as would the increased clearances of the larger bearings (Teoh et al., 2002). However, detailed inspection of the back surfaces of the remaining liners did not indicate any damage in these bearings.

Table 4:13: Summary of design differences between 28 and 52 mm diameter metal-on-polyethylene bearings

Design Parameter	28 mm bearings	52 mm bearings
Liner thickness, mm	10.20-11.40	3.00
Locking mechanism	Notches on the side of liners	Rosette locking at the bottom of the liner
Offset of centre of the inner diameter from the edge, mm	-2.43	0.00
Clearance, μm	100-450	325-681

Despite these design differences and different wear rates, the wear behaviour of the bearings appeared similar under standard simulator conditions. All liners, regardless of size, showed the same highly polished wear area within which light scratching could be observed suggesting abrasive wear mechanisms as described widely previously (McKellop, 2007, Sorimachi et al., 2009). The generation of polyethylene particles size distributions similar to those reported widely also suggests a similar wear mechanism. Both diameter bearings produced mainly spherical shaped particles, with 38 and 48 % of particles sized between 0.1- 0.2 μm for the 28 and 52 mm diameter bearings, respectively. Particles generated in crosslinked polyethylene have been reported to include fibrils and small granules (Galvin et al., 2010) as in the current study. The observation of nanometre sized particles (27 and 21% of the particles generated in the 28 and 52 mm diameter bearings) has been reported elsewhere for crosslinked polyethylene with 71% of particles produced in metal-on-polyethylene crosslinked at 95 kGy below 0.1 μm (Galvin et al., 2010). This represents a greater number of nanometre sized polyethylene particles in the crosslinked polyethylene but may be due to the different particle extraction protocols used. In a study by Saikko et al., (2002), particles of spherical shape were reportedly generated in both conventional and crosslinked polyethylene but the introduction of crosslinking produced smaller particles, mean sized 0.23 μm compared to the 0.28 μm particles generated in conventional polyethylene. This suggests that vitamin-E included in crosslinked polyethylene has little influence on particle size distribution which correlates with a pin-on-plate study comparing virgin and vitamin-E containing polyethylene (Bladen et al., 2013).

Despite the low wear rates reported in crosslinked polyethylene with or without vitamin-E, the revision rate of larger (44 mm) diameter metal-on-polyethylene bearings has been reported to be higher than in smaller diameters according to the England, Wales and Northern Ireland National Joint Registry (2013). This may suggest there may be issues with the adoption of large diameters metal-on-polyethylene bearings which limit the lifespan of the bearing. However, the numbers of implants and retrievals was markedly smaller than other cohorts and the reason for revision was not stated making it difficult to determine whether this is due to increased wear or other causes.

4.4.3 The impact of adverse testing

Attempts to replicate the third body wear mechanism observed clinically (Tipper et al., 2000, Kusaba and Kuroki, 1997, Minakawa et al., 1998, Hall et al., 1997, Ito et al., 2010) have used various third body particles added to the test fluid. The most commonly used are bone cement and alumina. Bradgon et al (2003) added both bone cement and alumina particles at a concentration of 0.15 mg/mL and reported alumina particles to be the more severe addition. The current study found the inclusion of alumina particles was indeed more severe than bone cement, even when bone cement was added at a higher concentration, 33 times greater than the concentration of alumina particles. The introduction of bone cement as a third body abrasive did increase the wear rates in large and small diameter bearings with similar wear rates achieved in the first third of a million cycles. This suggests that in the short term, third body abrasives may be more adverse in smaller diameters. The wear rates of the small diameter bearings became steady state and ultimately doubled compared to standard wear rates; the same increase was observed throughout testing with larger diameters. The introduction of bone cement in 95 kGy crosslinked polyethylene has reported wear to not be statistically significant with diameter over 5 million cycles of testing with no wear measured (Bragdon et al., 2005) but this may be due to the low (0.15 mg/mL) concentration of bone cement added. A higher concentration (5 mg/mL), comparable to the current study reported wear rates of 118.75 ± 35.33 mm^3/mc in 32 mm diameter liners irradiated at 105 kGy

(Wang and Schmidig, 2003), substantially higher than the wear rates of 14.87 ± 4.01 and 32.76 ± 9.90 mm^3/mc in the 28 mm and 52 mm diameter bearings reported in the current study, Figure 4:45. The wear rates in the current study are comparable to those reported in 32 and 44 mm diameter ceramic-on-polyethylene bearings under the same conditions (Wang and Schmidig, 2003, Kubo et al., 2009) highlighting the low wear possible in metal-on-vitamin-E blended highly crosslinked polyethylene.

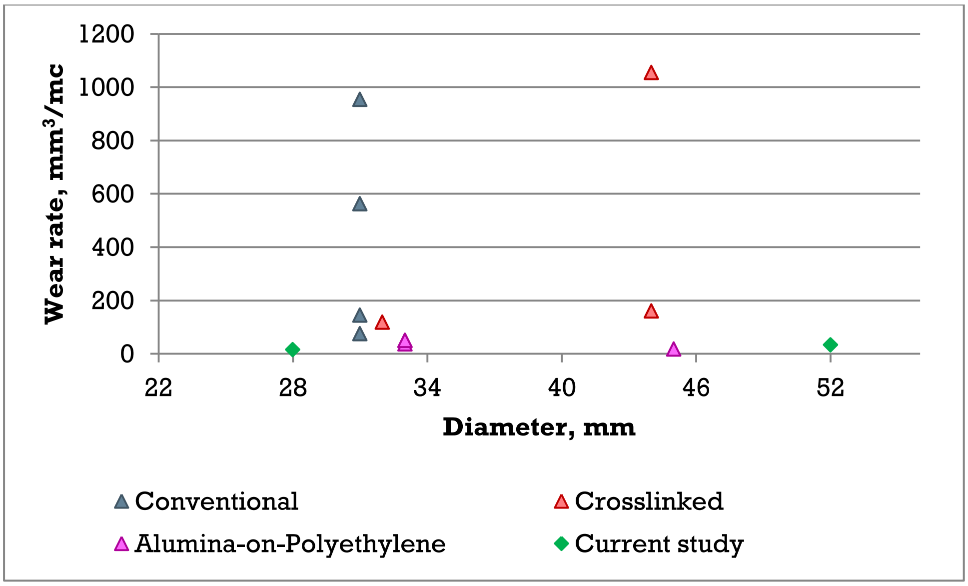


Figure 4:45: Wear rates reported in the literature with bone cement added a concentration of ≥ 5mg/mL compared to the results presented in this thesis.

In contrast, the inclusion of the alumina particles in the current study resulted in metal-on-polyethylene wear rates of 159.81 ± 108.55 mm^3/mc over the first one million cycles. Unlike in the bone cement test where the wear rate remained constant or decreased with time, the wear rate in the alumina test increased with each gravimetric interval and over the final third of a million cycles the wear rate was 368.65 ± 202.26 mm^3/mc; the longer the test with alumina third body particles, the more severe it became leading to a high reported standard deviation as it was not at equilibrium for these data points used. The wear rates produced in the 52 mm diameter metal-on-polyethylene bearings with 0.15 mg/mL alumina added to the test fluid were comparable to 32 mm diameter conventional polyethylene under the same conditions (Bragdon et al., 2004), Figure 4:46. Crosslinking has been shown to be resistant to this damage with wear rates of 39 and 48 mm^3/mc in 28 and 32 mm diameter bearings (Bragdon et al., 2003, Bragdon et al., 2004). The wear rate reported in the current study is larger than any reported in the literature for crosslinked polyethylene but the bearing diameter is also greater; the values are within reasonable expectations.

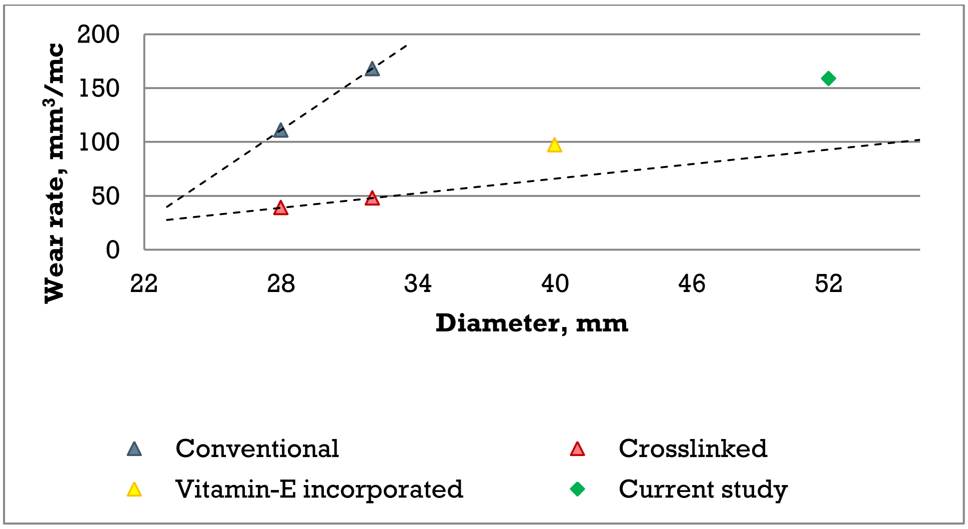


Figure 4:46: Wear rates with 0.15 mg/mL of alumina particles added to the test fluid from the current test and literature showing the trend of increasing wear with diameter

The high wear rate in the bearings tested with alumina particles also appeared to change the wear mechanism from adhesive, with light scratching originally observed on these liners under the standard test conditions, to abrasive, with heavier scratches. Wear particles generated under third body test conditions have not been reported previously, but in the current study displayed a high number of significantly smaller particles (less than 0.1 μm in size). These smaller particles may be more bioactive, although particles smaller than 50 nm are possibly too small to be reactive (Liu and Tipper, 2013). The bone cement third body test condition did not show significant changes in wear mechanism with the maintenance of the light scratching on the bearing surfaces and no changes in wear particles distribution produced.

It has been established that polyethylene wear is susceptible to roughened head counterfaces (Bowsher and Shelton, 2001, Barbour et al., 2000, Lee et al., 2009) and the current study suggests roughening may also influence vitamin-E blended highly crosslinked polyethylene. According to ISO-7206-2 (2011), the Ra roughness of metal bearing surfaces in total hip replacements at implantation should be less than 0.05 μm. Retrievals have reported roughening and scratching of the head in metal-on-polyethylene bearings and have shown Ra measurements of 0.17 ± 0.32 μm in Charnley prostheses (Haraguchi et al., 2001). Equally, Ito et al., (2010) reported the Ra of heads revised for osteolysis to show an increase to 0.19 ± 0.13 μm, Table 4:14. In dislocated bearings, representing severe damage with the heads contacting non-bearing surfaces, the Ra of the heads had increased to 0.3 - 0.5 μm, a significant change in the roughness (Ito et al., 2010, Mai et al., 2010). As dislocation is a leading cause for revision, producing this increased level of roughness may be clinically relevant as a method of accelerating wear and possibly representing an additional adverse test condition.

Table 4:14 : Surface roughness parameters of metal-on-polyethylene retrievals (dislocated bearings in italics) compared with the roughness achieved during third body testing in this thesis (in bold)

Mean Ra ± sd (range), μm	**Mean Rt ± sd (range), μm**	**Mean Rz ± sd (range), μm**	**Study**
0.02 ± 0.005			Tipper et al (2000) Low damage bearings
0.74 ± 0.89			Tipper et al (2000) High damage bearings
(0.013-0.037)	(0.041-0.086)		Raimondi et al (2001)
			Minakawa et al (1998)
	0.1-2.0 scratches		Jasty et al (1994)
0.062 (0.041-0.080)	1.08 (0.82-1.55)		Hall et al (1997)
0.12 ± 0.11 (0.01-0.45)		1.00 ± 0.77 (0.07-3.46)	Ito et al (2010)
0.380 ± 0.308			*Eberhardt et al (2009)*
0.307			*Mai et al (2010)*
0.56 ± 0.12 (0.41-0.81)		*3.98 ± 0.91 (3.05-6.37)*	*Ito et al (2010)*
0.028 ± 0.010 (0.021-0.066)	**2.859 ± 0.883 (1.698-4.204)**	**1.799 ± 0.730 (0.873-3.404)**	**Current Study 28 mm Ø Bone Cement particles**
0.024 ± 0.006 (0.013-0.041)	**2.796 ± 0.920 (1.416-4.562)**	**1.820 ± 0.646 (0.812-3.616)**	**Current Study 52 mm Ø Bone Cement particles**
0.018 ± 0.010 (0.006-0.049)	**4.756 ± 1.762 (2.748-8.592)**	**2.730 ± 1.127 (0.877-4.850)**	**Current Study 52 mm Ø Alumina particles**

The average roughness, Ra, however is only one surface parameter and considers the average of absolute values, Figure 4:47. Increases in the peak and valley surface profile may not be addressed, with other roughness parameters actually better representing the distance between the surface peak and valleys. These may include the peak height from the mean, Rp, the maximum distance between peaks and valleys over an entire evaluation length, Rt, or the mean distance between the maximum peak and valley over a sampling length, Rz. In stylus measurements Rt and Rz may be the same (Cohen, 2014). These surface parameters are less commonly used and are not well prescribed in the manufacturing process. Only Rt is described in ISO-7206-2 (2011) as being required to be less than 1 μm. Retrievals appear to have shown little change in the Rt roughness parameter although many studies have not measured this,

Table 4:14. Other parameters such as Rz, measured in retrievals following aseptic loosening and osteolysis have displayed Rz of 1.00 ± 0.77 μm with dislocation producing a higher Rz of 3.98 ± 0.91 μm (Ito et al., 2010). A simulator study considering roughened heads (Galvin et al., 2008) has observed no correlation between Ra and polyethylene wear. This was also observed in the current study with increasing wear despite no change in Ra. However, both Rt and Rp values did correlate to polyethylene wear with R^2 values of 0.727 and 0.621 respectively (Galvin et al., 2008) and indeed, the greater head Rt values reported in the current study showed higher polyethylene wear.

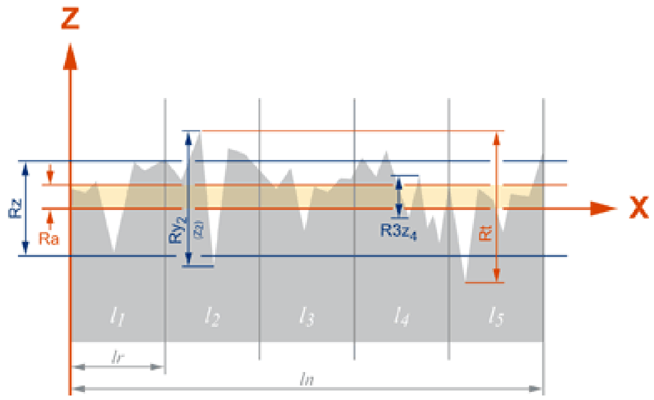


Figure 4:47: Diagram showing Ra, Rz and Rt surface roughness parameters. Image taken from Aro-Tec GmbH (2010)

Others have suggested that the roughness achieved in the heads is not as influential as the area of roughening (Bowsher et al., 2008). Jasty et al., (1994) reported surface damage over 25% or more of retrieved heads in approximately 67% of retrievals. The generation of several distinct scratches for *in vitro* testing may not fully replicate the roughening observed clinically, as the area of the head which is damaged is much less than in retrievals, yet these have produced increased Ra values (Lee et al., 2009, Barbour et al., 2000). In the heads tested in the current study, the Rt and Rz values measured were higher (1.10-5.19 μm and 0.06-5.64 μm respectively) before testing than stated in ISO 7206-2 (2011), probably as a result of the method of surface roughness measurement. The Rt value of 1.0 μm as specified by the standard, is measured using a stylus which is often unable to measure the full depth of the valleys. The use of an optical surface profilometer, however, can measure these with more precision resulting in higher Rt values. The Rt and Rz values did not significantly change from the initial testing and after bone cement third body testing. The use of alumina particles, however, produced Rt values comparable to scratched areas in heads with titanium deposits (Patten et al., 2010). The elevated Rz values of these heads, however, were still within the range reported in retrievals due to osetolysis (Ito et al., 2010). The use of hard third bodies in the test fluid may be a highly relevant roughening model which affects both surfaces yet there remains an element of variability, as observed in the current work. In the bearings tested in this thesis, higher wear rates occurred after the removal of the alumina third body particles with the articulating surfaces damaged, suggesting that damage to the metal counterface in metal-on-polyethylene bearings may be of greater significance in terms of adverse testing than 3rd body mechanisms as long as sufficient damage is produced.

While generating damage to the counterface clearly influences the wear rate of polyethylene, third body particles have also been reported to embed into the surfaces of both metal and polyethylene bearings (Klapperich et al., 1999, Sychterz et al., 1996). Several third body particles have been reported including bone, bone cement, titanium and hydroxyapatite originating from dislocation or loosening of components or generated during the surgical procedure (Morsher et al., 1998, Davidson et al., 1994) with up to 70% of polyethylene retrievals showing embedding (Hess et al., 2013). The current study has shown embedding of both bone cement and alumina third body particles in both metal and polyethylene surfaces *in vitro* however, the influence on the wear of these material combinations was different dependent on the particles themselves. Bone cement has previously been reported to embed in polyethylene (Wang and Essner, 2001) and metal (Sorimachi et al., 2009) although no increase in polyethylene wear rate has been reported when these particles are removed from the test fluid. The bone cement particles may in fact protect the polyethylene from contact with the head surface acting as a solid lubricant. In the current study, the presence of bone cement particles also produced reductions in cobalt release compared to standard test conditions, although this was only statistically significant in the smaller sized bearings, suggesting that the particles were either not hard enough or were not embedded in a large enough quantity to produce significant scratching on the heads. In the metal bearings tested with bone cement particles added to the test fluid, it has been proposed previously that the adhesion of these particles onto the bearings surfaces prevents ion release (Saikko et al., 1998). This appears to have occurred in the 28 mm diameter bearings of the current study.

The alumina particles also embedded into both bearing surfaces of the metal-on-polyethylene bearings and led to increased polyethylene wear when these particles were removed from the test fluid. In another study considering 28 mm diameter metal-on-conventional polyethylene bearings tested with alumina particles at a concentration of 0.15 mg/mL, a higher wear rate of 13.5 ± 3.7 mm^3/mc was observed after 2 million cycles of testing with alumina particles removed and new, pristine heads adopted compared to the initial wear rate (without particles) of 10.1 mm^3/mc (Bragdon et al., 2003). Although this wear rate was significantly lower than that reported following alumina third body testing in the current study (474.85 ± 470.35 mm^3/mc), only particles embedded in the polyethylene would have been present in the further testing rather than in the head and cup. Other studies have shown that with only 5 CoCrMo particles (300-320 μm diameter) embedded in conventional and 50 kGy crosslinked polyethylene, multiple scratches can be generated on the liner after only 10,000 cycles although this outcome is highly variable (Heiner et al., 2012).

The difference in the wear rates following the removal of the third body particles is attributed to the difference in the hardness between the bone cement and alumina. Davidson et al. (1994) observed the wear of metal, ceramic and polyethylene in a pin on plate study using different third body abrasives. It was determined that the hardness of the wear surface compared to the hardness of the third body particles was important in providing resistance to this abrasion. A wear surface 1.2 times softer than the abrasive was reported to result in increased wear and the harder third bodies becoming entrapped in the wear interface. Polyethylene, the softest of the three materials, therefore is the most susceptible to abrasive damage and embedding and the use of harder alumina particles would produce greater wear increases and embedding.

Jogging under the damaged and embedded conditions showed only a small increase in the wear rates which was not significantly different to wear rates under walking conditions. This contrasts reports of jogging under roughened conditions producing wear rates of 3123 mm^3/mc, an increase of 90 times compared to roughened walking conditions (Bowsher & Shelton, 2001). The heads in the current study displayed surface roughness Ra and Rt values within the lower limits of those recorded in the previous study and therefore it seems unlikely that any difference in surface roughness would be the cause for this difference in wear rate.

Similarly, no significant difference was observed with increased rotational speed in the current test yet a previous study has reported a power function relationship between wear and speed (Bowsher and Shelton, 2001). In both studies increasing rotational speed reduced the swing phase duration and moved the position of the heel strike by 18° and 27° from 1 to 1.5 Hz and 1 to 1.75 Hz respectively. The load cycle produced as different rotational speeds resulted in different swing phase load durations. One cycle of jogging at each frequency therefore represented different durations at which the load applied was greater than 300 N. In the 1 Hz case, the load remained at 300 N for approximately half of each cycle, longer than in the walking simulation. However, as the speed was increased to 1.5 and 1.75 Hz, the duration of loading at 300 N decreased to 25 and 12.5% of each cycle. The little difference in wear rates reported with increasing rotational speed suggest that vitamin-E highly crosslinked polyethylene may be less sensitive to changes in loading compared to the moderately crosslinked polyethylene tested in a previous study. This may also explain why the jogging wear rates in the current study are comparable to the slow jogging wear rate (319 mm^3/mc) reported by Bowsher & Shelton (2001).

4.4.4 Cobalt release and head wear in metal-on-polyethylene bearings

Wear and corrosion are possible in any bearing surface but in metal-on-polyethylene bearings, the emphasis is often on the wear of polyethylene as the wear particles produced are recognised to result in osteolysis (Lewis, 1997). However, it is possible that the metal heads can wear also, with instances of scratching on retrievals reported (Tipper et al., 2000) and elevated cobalt and chromium levels in the blood serum of patients who have received metal-on-polyethylene bearings (Hallab et al., 2004), although this has often been attributed to taper corrosion.

This study is the first to determine *in vitro* cobalt release and mass change of metallic heads in metal-on-polyethylene bearings even though wear was only measurable when larger diameters were used. In metal-on-metal bearings, the influence of diameter on metal ion release is under debate with some studies suggesting larger diameter bearings produce greater levels of cobalt and chromium (Clarke et al., 2003) while others have stated diameter does not have an influence (Daniel et al., 2006). In metal-on-polyethylene retrievals, a significant increase in taper corrosion scores have been observed with an increased diameter from 28 to 36 mm diameter (Dyrkacz et al., 2013) and therefore this would be likely to continue to a 52 mm diameter. Indeed, cases of pseduotumours have been reported in patients with larger diameter metal-on-polyethylene bearings (>40 mm) (Cook et al., 2013). The introduction of a larger head is believed to increase the torque between the head and taper as a result of greater friction at the bearing surface resulting in micromotion, fretting and corrosion.

In this study, clinically relevant tapers were used in all bearings and were not isolated therefore any cobalt release and volume loss could be generated either at the bearing surface or at the taper. However, the taper showed no visible damage throughout testing and as the tapers in all tests were not coated, cobalt would be expected to be comparable regardless of head surface. Very little cobalt was measured in the coated components which suggests that the majority of volume loss originated from the bearing surface. Despite measurable head wear in the metal-on-polyethylene bearings of this study, these wear rates were lower than reported steady state wear rates in metal-on-metal simulator testing (Royle, 2012); although metal-on-metal wear rates consider wear from both bearing surfaces. The cobalt released was also one to two orders of magnitude lower than metal-on-metal testing but was greater than soak controls in the uncoated bearings. The majority of cobalt measured was found to be ionic which could be because either the wear particles produced decomposed rapidly or a corrosion process occurred on the surfaces of these bearings or both.

In both diameters tested with bone cement, the cobalt release doubled even though permanent damage did not occur. This suggests that the bone cement may have produced fine scratches which did not influence the surface roughness but did remove some of the metal bearing surface. The use of these clinically relevant abrasives suggested potential for damage and increased cobalt levels in metal bearing surfaces. When these particles were removed, the cobalt release reduced from standard test levels in the small diameter bearings but remained elevated in the large diameter bearings possibly as greater levels of embedded particles in the polyethylene continued to scratch the heads.

The introduction of alumina third body particles increased the wear and cobalt levels of the large diameter bearings to levels greater than adverse metal-on-metal test conditions (Royle, 2012), representing significant removal of material from the bearing surface. The relationship established between cobalt levels and polyethylene wear in this study suggests that cobalt levels can be indicative of the head surface and therefore clinical levels may not only indicate increased risk of metal hypersensitivity reactions but also increased polyethylene wear possibly leaving to osteolysis. The alumina particles embedded in the polyethylene liners were sufficient to increase the cobalt released into the test fluid after these particles were removed from the test lubricant. Metal surfaces have also shown a vulnerability to abrasion in metal-on-metal bearings using cobalt chrome and titanium (Ti-6Al-4V) particles at a concentration of 0.0125 mg/mL (Halim et al., 2014). Titanium particles were observed to adhere and flatten onto the metal heads, suggesting that embedding of particles into metal surfaces may be an additional, clinically relevant adverse test condition with reports of embedded particles in retrieved metal bearing surfaces (Klapperich et al., 1999).

4.4.5 The use of chromium nitride coatings

Ceramic heads have been introduced as an alternative counterface but can be limited in bearing size and the bulk material remains brittle (Callaghan and Liu, 2009). Ceramic coatings on metal bearing surfaces have been investigated in metal-on-metal bearings but there have been several reports of failure *in vitro* (Leslie et al., 2013, Royle, 2012). Coatings have also been developed for metal-on-polyethylene bearings but little improvement in polyethylene wear rate has been reported under standard test conditions (Galvin et al., 2008). This is because it is often difficult to produce surface finishes smoother than the metallic surface, especially using physical vapour deposition methods which produce microdroplets. The CrN coating investigated in this current study produced comparable rather than improved wear rates under standard conditions in the 52 mm diameter heads to the uncoated metal-on-polyethylene under standard conditions suggesting that the polyethylene has been enhanced to a point where it is difficult to establish differences in head type under standard conditions.

Under adverse conditions, however, the benefits of a coating became more apparent, producing lower wear rates than the metal-on-polyethylene bearings and preventing runaway wear in a similar fashion to ceramic-on-polyethylene bearings (Wang and Schmidig, 2003). The CrN coating was tested in the presence of alumina third body particles which damaged the uncoated metal heads but the increased scratch resistance of the coating prevented this permanent damage and good adhesion of the coating was demonstrated. An increase in polyethylene wear was reported during third body testing but the removal of these particles reduced the wear rate to that observed in the initial standard conditions. The increased wear rate during the third body testing was due to the presence of the third body particles alone which have shown to produce increased wear without significant damage in the bone cement testing of the current study. The low wear rates reported may also be due to the increased hardness of the coating preventing embedding of the alumina particles on the heads as has been reported in ceramic heads with bone cement (Wang and Essner, 2001). The robust nature of the coating also prevented the generation of smaller, more bioactive particles.

The study highlights the potential for head wear and cobalt release in metal-on-polyethylene bearings which have seen disastrous clinical effects in metal-on-metal bearings (Pandit et al., 2008). Reduction of cobalt would therefore be beneficial in these bearings with growing reports of pseudotumours in metal-on-polyethylene bearings (Cook et al., 2013). It has been shown that the CrN coating acts as a barrier to cobalt release only producing amounts comparable to soak controls in all stages of testing. This cobalt barrier behaviour has been noted in several studies on metal-on-metal bearings (Royle, 2012, Fisher et al., 2004) but until now, not investigated in metal-on-polyethylene bearings. CrN coatings may not only reduce the risk of increased polyethylene wear rates but also minimise any potential adverse tissue reactions due to metal corrosion products in large diameter bearings.

4.5 Conclusions

Vitamin-E blended highly crosslinked polyethylene is capable of producing low wear rates even in large diameters under clinically relevant adverse conditions. Cobalt release, however, is measurable in all metal-on-polyethylene bearings and increases with increasing diameter which may present an additional challenge in utilising large diameter metal-on-polyethylene bearings. The use of a CrN coating on the metal bearing surface offers an attractive alternative allowing large diameter metal-on-polyethylene bearings to be utilised. This coating acts as a cobalt barrier, preventing ionic release, and the increased scratch resistance of the coating may prevent increases in polyethylene wear due to third body abrasives and damage, as observed in the uncoated bearings.

5 Silver Chromium Nitride Coated and Uncoated Metal-on-Metal Bearings under Standard and Rim Contact Conditions

5.1 Introduction

In recent years, cases of pseudotumours, ARMD and hypersensitivity reactions have been widely reported in patients receiving metal-on-metal hip replacements (Pandit et al., 2008, Langton et al., 2010). Elevated cobalt concentrations have been observed in the blood and urine of those affected and suggested as a potential cause of the phenomenon reported (Jacobs et al., 2004). Standard hip simulator tests have underestimated the wear and ion release experienced clinically and possibly more significantly, the extreme biological reactions to the products of the wear process. The effects have led to increased revision rates, high metal wear rates and elevated blood ions in many patients often with increased (greater than 50°) inclination angle (Hart et al., 2011). This angle has been adopted as a recognised form of adverse testing (Angadji et al., 2009) although the particular design of these bearings can influence the wear response to this adverse test condition, with some bearings reporting high wear at high inclination angles due to a reduced coverage arc and others reporting no statistical significance from standard testing (Leslie et al., 2009b, Royle, 2012). The introduction of lateralisation to produce rim contact, has also been shown to lead to further increased wear rates (Al-Hajjar et al., 2013b) with the majority of metal-on-metal retrievals, i.e. those that have experienced clinical failure, exhibiting edge loading (Matthies et al., 2011a).

One proposed solution to the problem of metal wear, corrosion and metal ion release is to coat the bearings surfaces with a ceramic such as chromium nitride

(CrN). This has been used in a number of previous studies utilising physical vapour deposition (PVD) techniques (Fisher et al., 2004, Royle, 2012). Coatings have performed well in standard hip simulator tests with low steady state wear rates of 0.1 mm^3/mc (Williams et al., 2004a) or below (Royle, 2012). However, adverse test conditions have highlighted not only the potential for increased wear, but have shown failure of coatings under lateralisation conditions. Delamination of arc evaporative PVD CrN coatings has been reported leading to steady state wear rates of 18.04 ± 27.65 mm^3/mc (Leslie et al., 2013), demonstrating how failure of a coating can be catastrophic Increased wear rates of EBPVD CrN coatings has been reported after testing following 50 cycles of subluxation damage. In one bearing this was attributed to cohesive failure of the coating while the remaining bearings exhibited this increased wear due to roughening of the bearing surfaces (Royle, 2012).

The inclusion of silver into the EBPVD CrN coatings has been proposed to further reduce wear whilst potentially offering an antimicrobial effect (Monteiro et al., 2009). Different concentrations of silver have been added to these coatings (17, 41 and 51 wt%) and different coating structures have been investigated. The increased silver concentration in the CrN coatings exhibited decreased run-in wear from 0.74 ± 0.22 mm^3/mc to 0.67 ± 0.19 mm^3/mc under standard conditions but low steady state wear rates (less than 0.11 mm^3/mc) were reported in all silver CrN coatings (Royle, 2012). The inclusion of 51 wt% silver in a homogenised EBPVD CrN coating has proven resistant to adverse testing of damage and high inclination angle conditions (Royle, 2012), yet has not been thoroughly tested under lateralisation conditions. Other variables in these coatings, such as grading to produce different levels of silver at the surface, can be introduced but have not been previously investigated.

The study focuses on the wear and cobalt release of metal-on-metal bearings with the removal of the swing phase load and introduction of cup displacement leading to edge loading. It explores the potential for silver containing chromium nitride coatings with differing silver surface content to reduce the wear and cobalt release without delamination or cohesive failure under these adverse conditions.

5.2 Materials and Methods

5.2.1 Test components and conditions

As-cast, hot isostatically pressed and solution annealed CoCrMo, as described in ASTM F75-12, was manufactured as 48 mm diameter head and cups (Corin, UK). Sixteen heads were taken from manufactured stock while the cups were custom made to feature a cylindrical peg on the back to allow for mounting, Figure 5:1. Nine pairs remained uncoated while seven were coated with 51wt% Ag and CrN via EBPVD at a thickness of approximately 8 μm. In the coating process, the heads and cups were cleaned and initially coated with 0.2-0.5 μm of a chromium adhesion layer before Ag-CrN was added. Four of the coated components were graded to be silver rich at the surface of the bearings while the three were graded to have very low levels of silver at the surface.

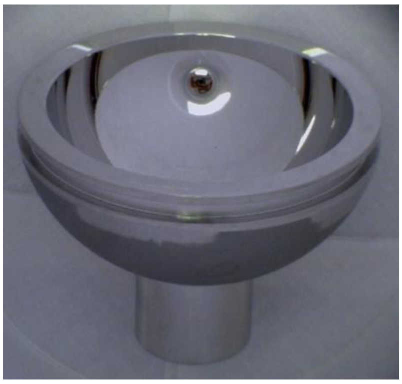


Figure 5:1: Photograph showing custom made CoCrMo cups with cylindrical peg for testing

Four uncoated pairs (MoM S1-4) were tested under standard test conditions, Table 5:1, as described in ISO 14242-3 (2009). These were tested for 2 million loading cycles (mc) with gravimetric wear determined at 0.17, 0.33, 0.67, 1.00 and 2.00 mc. The remaining five uncoated bearings were tested with the swing phase load removed up to 5 mc to provide a 1 mm separation between head and cup. Three uncoated cups (MoM+L1-3) were displaced using the spring mechanism (+L) described in section 3.1.5 to produce 0.7 mm of medial movement of the cup while the remaining two uncoated MoM (MoM-L1 and MoM-L2) were not (i.e. separation with no lateralisation (-L)). The same gravimetric intervals were taken as the standard test conditions and every million cycles thereafter. Volumetric wear was determined from mass loss using the density of 8300 kg/m^3 for CoCrMo.

The silver rich (Ag+) surface coated components (CrN-Ag+1-4) were tested for 0.17 million cycles under standard conditions. Three of the silver rich cups were then rotated to unworn areas and tested for a further 0.17 million cycles. The silver depleted (Ag-) surface coated components (CrN-Ag-1-3) were tested for 5 million cycles under lateralised conditions (separation and lateralisation conditions) for 5 million cycles. Following this, two of the cups were rotated and these bearings were run for 0.17 million cycles under standard conditions. The volumetric wear of these bearings was determined from the mass loss and density of 9000 kg/m^3 for silver chromium nitride.

Table 5:1: Summary of test components, clearance data provided from Corin Ltd, UK

Bearing	Coated/Uncoated	Clearance, µm	Test condition
MoM S1	Uncoated	195	Standard 2mc
MoM S2	Uncoated	203	Standard 2mc
MoM S3	Uncoated	215	Standard 2mc
MoM S4	Uncoated	191	Standard 2mc
MoM-L1	Uncoated	155	Removed swing phase 5 mc
MoM-L2	Uncoated	157	Removed swing phase 5 mc
MoM+L1	Uncoated	154	Lateralised 5 mc
MoM+L2	Uncoated	150	Lateralised 5 mc
MoM+L3	Uncoated	151	Lateralised 5 mc
CrN-Ag+1	CrN-Ag coated, increasing Ag at surface	155	Standard 0.17 mc, Cup Rotated standard 0.17 mc
CrN-Ag+2	CrN-Ag coated, increasing Ag at surface	152	Standard 0.17 mc, Cup Rotated standard 0.17 mc
CrN-Ag+3	CrN-Ag coated, increasing Ag at surface	171	Standard 0.17 mc, Cup Rotated standard 0.17 mc
CrN-Ag+4	CrN-Ag coated, increasing Ag at surface	174	Standard 0.17 mc
CrN-Ag-1	CrN-Ag coated, depleting Ag at surface	143	Lateralised 5 mc, Cup Rotated standard 0.17 mc
CrN-Ag-2	CrN-Ag coated, depleting Ag at surface	155	Lateralised 5 mc
CrN-Ag-3	CrN-Ag coated, depleting Ag at surface	152	Lateralised 5 mc, Cup Rotated standard 0.17 mc

5.2.2 Ionic release

All fluid was collected throughout testing as well as 15 mL samples taken at approximately 3, 6, 12 and 24 hours correlating to 10,800, 21,600, 43,200 and 86,400 cycles respectively. From this fluid, 0.2 mL was used to determine the total cobalt concentration (ions plus particles) produced from each station during testing as described in section 4.2.4. At the end of each test or at 0.33 mc and 1.5 mc, 15 mL fluid samples were taken and centrifuged at 165,000 *g* for 3 hours using a 70Ti rotor (Beckman Coulter, UK). The supernatant was removed and analysed for cobalt concentration to give the ionic cobalt concentration. In the coated components, the fluid collected was also used to measure the amount of silver released throughout testing in the same manner as cobalt.

5.2.3 Particle isolation

The pellet produced during the centrifugation of the test fluid was used to characterise the particles produced following the method described by Billi et al (2011b), Appendix D. The supernatant was removed leaving only 2 mL and the pellet which was then digested with urea, HEPES, sodium azide and proteinase K. A copper grid was then placed at the bottom of a test tube and caesium trifluoroacetate was added. This was spun for 15 minutes at 30,000 *g* before the metal particle fluid was added and spun at 3,300 and 84,000 *g* for 30 minutes and 4 hours respectively using a MLS-50 rotor (Beckman Coulter, USA). The copper grid was allowed to dry and placed in a transmission electron microscope (JEM-2010, Jeol Ltd, Japan) to view the particles. Ten images comprising of a minimum of 100 particles in total were recorded and analysed using Image Pro Plus (Media Cybernetics, USA) to determine particle size and distribution.

5.2.4 Surface analysis

Head surfaces were inspected using a scanning electron microscope (Inspect F, FEI, Eindhoven, NL) by mounting the heads on a custom made fixture before and after testing to study the microscopic surface features. Macroscopic images of the heads and cups were also taken using a USB microscope (VMS-004 Discovery Series 400x, Veho, Hampshire, UK). These images were used to estimate the wear area based on a projection method previously developed (Ward, 2011). The USB microscope was also used to image the wear regions of the cups.

Following lateralisation tests, the wear stripe produced on the heads was measured by an optical surface profilometer (Bruker, USA) using a backscanning green light filter and a 20 x lens. From this profile, the depth of these stripes was ascertained.

5.3 Results

5.3.1 Metal-on-Metal bearings under standard conditions and with the swing phase load removed

The metal-on-metal bearings tested under standard conditions predominantly showed a tri-phasic wear pattern with the majority of wear occurring within the first third of a million cycles. One bearing (MoM S4) showed the same wear trend but with an increased transition wear phase while another (MoM S3) exhibited a higher steady state wear rate, Figure 5:2. The removal of load during swing phase produced different wear behaviour. One bearing (MoM-L2) showed no run-in or transition phase with mass gain in the initial 0.17 mc and then consistently produced a wear rate averaging 0.60 ± 0.03 mm^3/mc. The other bearing showed a prolonged run-in to 0.67 mc and then wear reduced. The removal of swing phase load resulted in a significant ($p<0.05$) decrease in the run-in wear (0-0.33 mc) but no significance ($p>0.05$) was found in the transition (0.33-1.00 mc) and steady state (1.00-2.00 mc) wear rates compared to standard conditions, Table 5:2. This increased wear in the swing phase load removed bearings was attributed to uncontrolled rim contact during heel strike producing additional damage in head and cups. The rim contact was the result of the separation caused by the removal of swing phase load producing a misalignment of the head with the cup (as the cup moves a small amount to self-align with the head during standard testing).

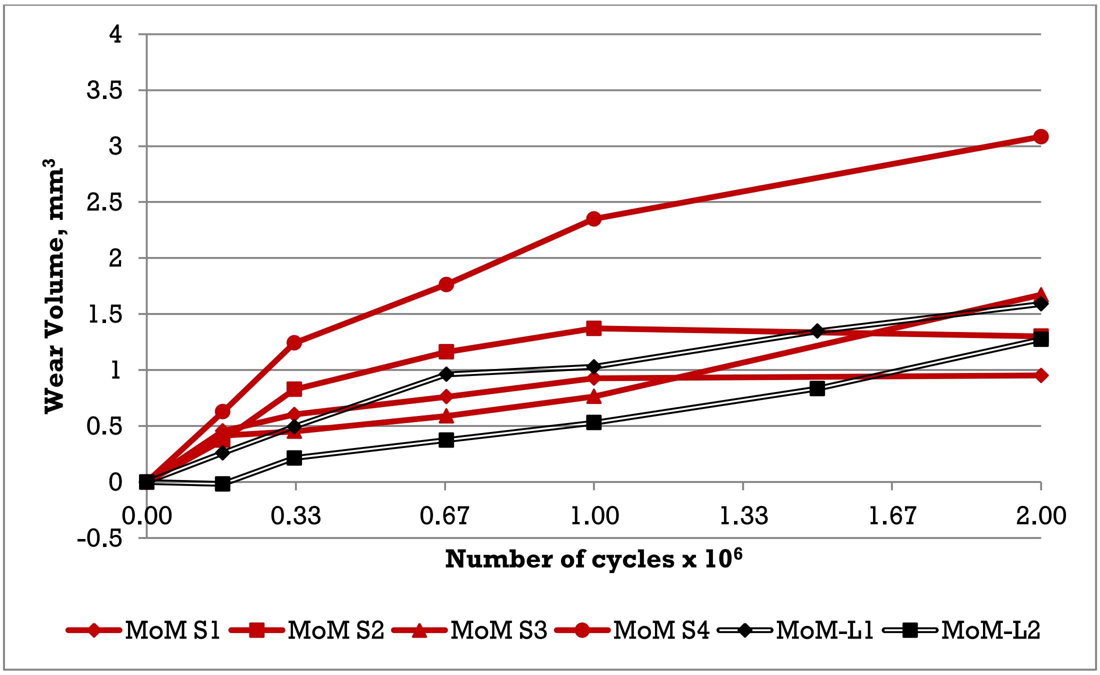


Figure 5:2: Metal-on-metal cumulative volume loss during standard conditions (S) and with the removal of swing phase load (-L) over 2 million cycles

Table 5:2: Mean run-in (0-0.33 mc), transition (0.33-1.00 mc) and steady state (1.00 -2.00 mc) wear rates for metal-on-metal bearings under standard and removed swing phase load conditions

Conditions	Number	Wear rate, mm^3/mc		
		Run-in	Transition	Steady State
Standard	4	2.65 ± 1.19	0.81 ± 0.53	0.40 ± 0.49
Reduced Swing Phase Load	2	1.06 ± 0.59	0.64 ± 0.23	0.70 ± 0.09

Although the wear of the standard bearings was consistent during these tests, the proportion of wear on the head and cup differed, Figure 5:3. One bearing (MoM S1) produced no measurable head wear throughout testing while another bearing (MOM S4) produced between 22-26% of the total wear from the head. No significant difference ($p>0.05$) was observed in the proportion of head wear during the progression of the standard test. The removal of swing phase load did not alter this behaviour with no significant increase ($p>0.05$) in the proportion of head wear over 2 million cycles. Under both test conditions, it was found that an increase in total wear was accompanied by an increased proportion of head wear.

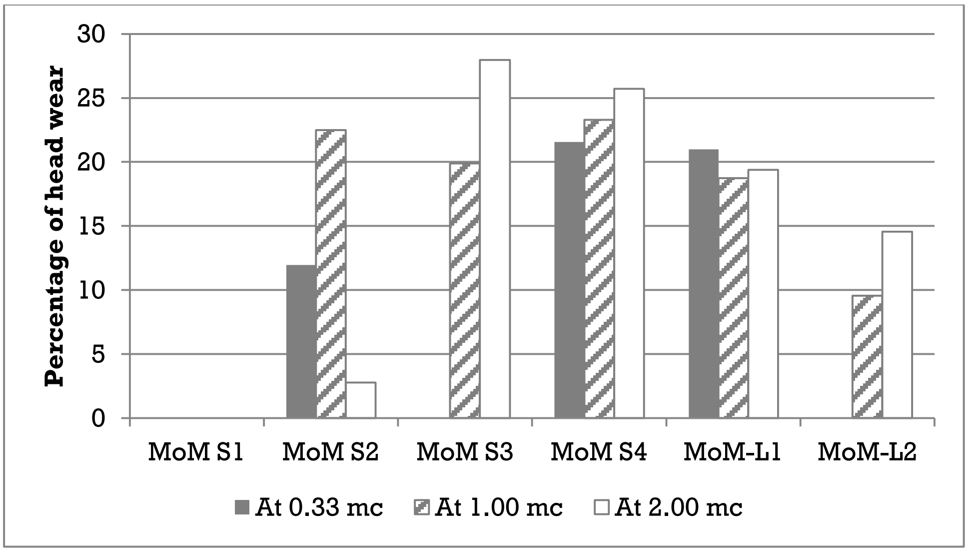


Figure 5:3: Head wear as a percentage of total wear in metal-on-metal bearings during each wear phase

Head wear in the standard conditions tested bearings was observed to increase over the first million cycles of testing, Figure 5:4a. Two heads (MoM S1 and MoM S2) then reported mass gain between 1 and 2 mc while the other two heads continued to wear. In all instances, wear was low (below 0.8 mm^3) over 2 million cycles. The heads tested without a swing phase load produced two thirds of the wear reported under standard bearings after 2 million cycles, Figure 5:4b. The lower head wear in the swing phase load removed heads was combined with a smaller wear area; approximately 36% of the total surface of the standard heads showed wear features while only 21% of the swing phase removed heads.

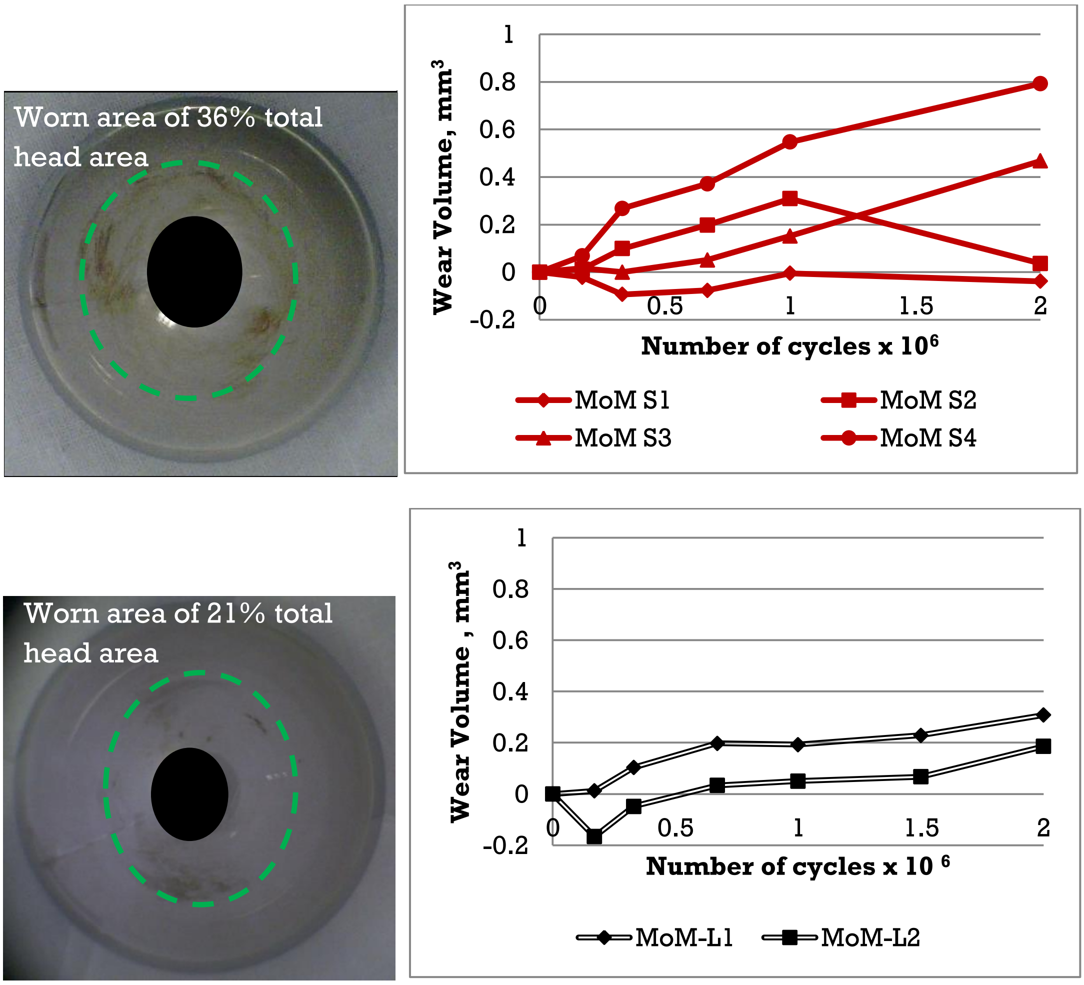
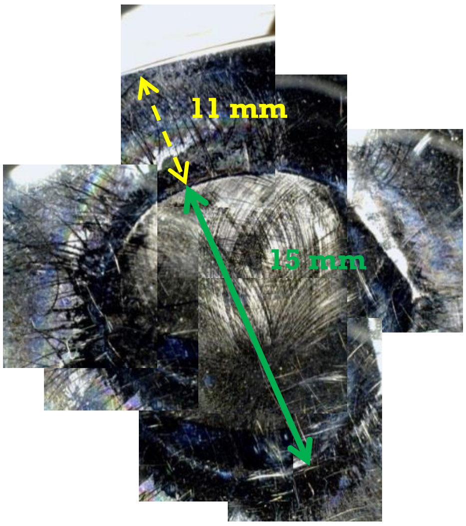
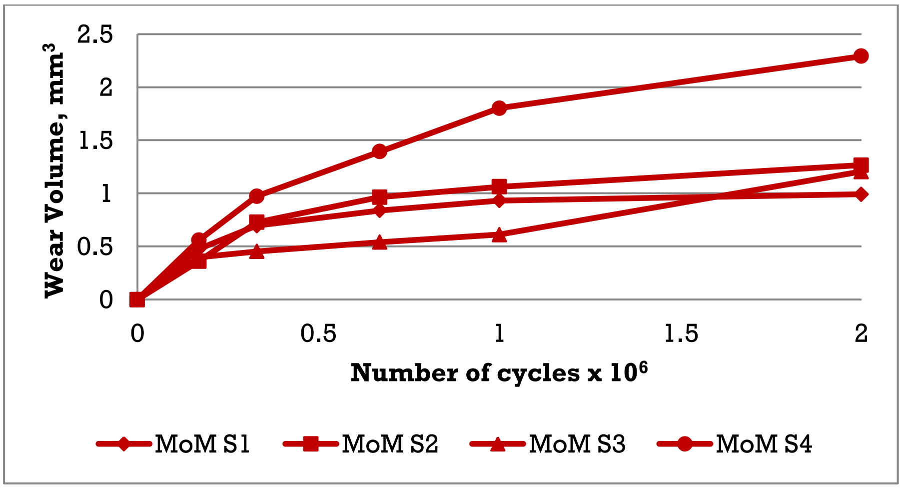


Figure 5:4: Image of head and wear volume loss of head alone after 2 million cycles of (a) standard testing and (b) with the swing phase load removed. Wear patches are highlighted by dotted lines (reflection removed from the centre of each bearing)

The wear in the cups under standard conditions occurred within a smaller contact area than the head wear with the generation of a circular wear patch of approximately 15 mm in diameter, Figure 5:5a. Greater wear (>1 mm^3) was measured in the cups than the heads, Figure 5:5b, and showed the same tri-phasic wear trend observed in the total wear.



a



b

Figure 5:5: MoM under standard test conditions producing (a) typical wear patch after 2 million cycles and (b) gravimetric wear of the cups

Wear in the cups under swing phase load removed conditions, also produced a circular wear patch but this was smaller than the standard conditions wear patch, Figure 5:6a. A small amount of damage was observed at the rim of the cup in the swing phase load removed bearings. This may have increased cup wear leading to comparable wear between standard and removed swing phase load conditions after 2 million cycles.

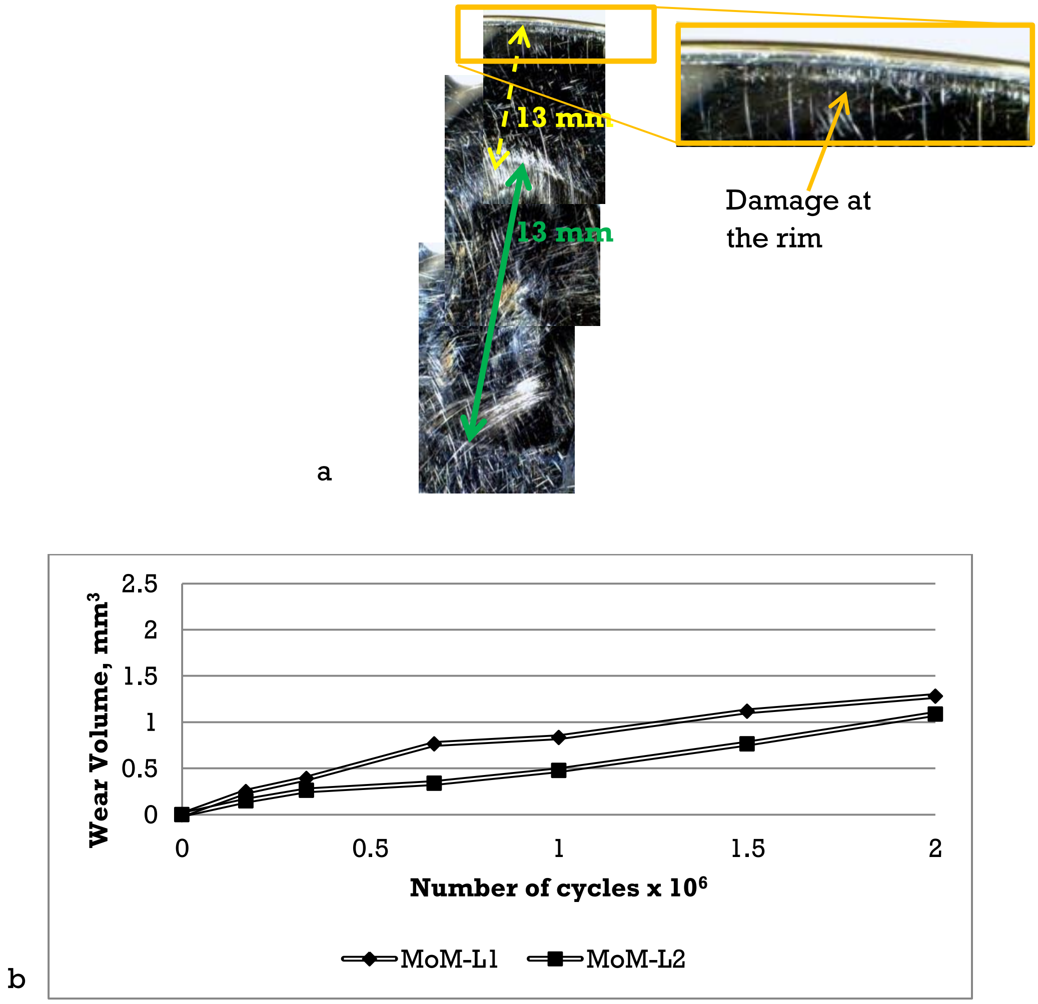
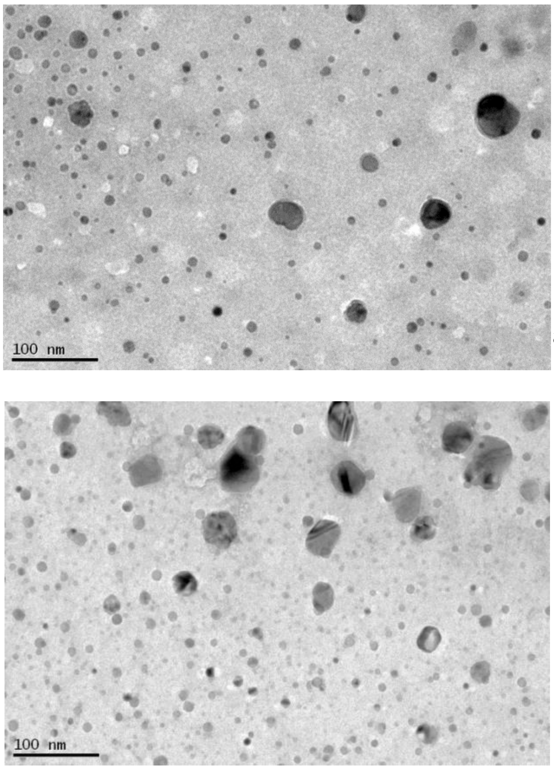


Figure 5:6: Acetabular cup (a) wear patch and (b) wear volume over 2 million cycles testing with the removal of swing phase load

The appearance of the wear particles generated with the different swing phase loads was similar, Figure 5:7. This was reflected in the particle distributions which showed the majority of particles to be sized less than 40 nm, Figure 5:8. No significant difference ($p>0.05$) was observed between the standard particles and the swing phase load removed particles with a mode of 14 nm compared to 13 nm. Slightly more particles between 100 and 500 nm were found under standard conditions compared to the swing phase load removed conditions which produced more particles between 60-100 nm.



a

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Figure 5:7: Wear particles produced during (a) standard conditions and (b) the removal of swing phase

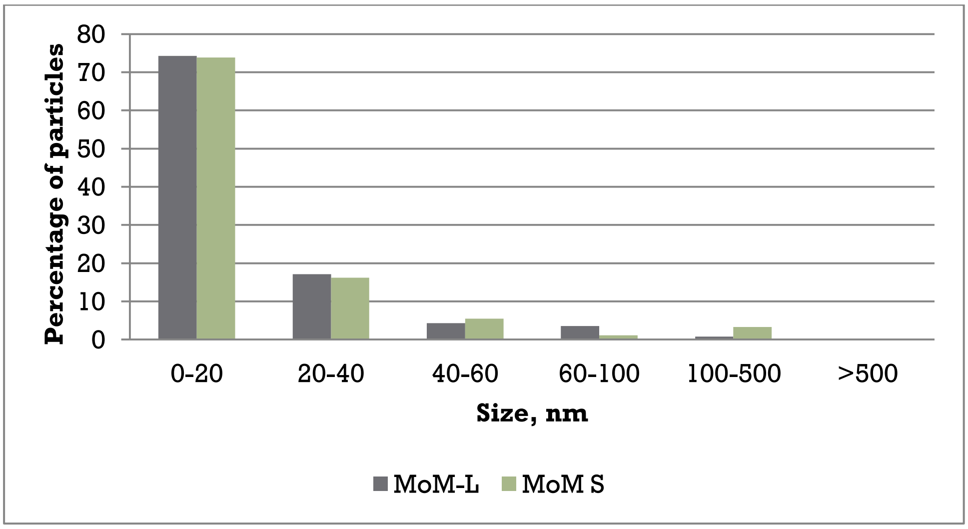

Figure 5:8: Particle distribution of the metal particles produced under standard and removed swing phase load conditions showing comparable distributions

Cobalt released into the test fluid showed a similar trend to the gravimetric total wear loss. An initial large amount of cobalt was released within the first third of a million cycles under standard conditions producing more than the removed swing phase load conditions, Figure 5:9. However, unlike wear, as testing continued, the rate at which cobalt was released under standard conditions remained greater than that observed with the removal of the swing phase load except for in one bearing (MoM S1) which produced very little cobalt after 0.33 million cycles. This bearing also produced little wear during this period.

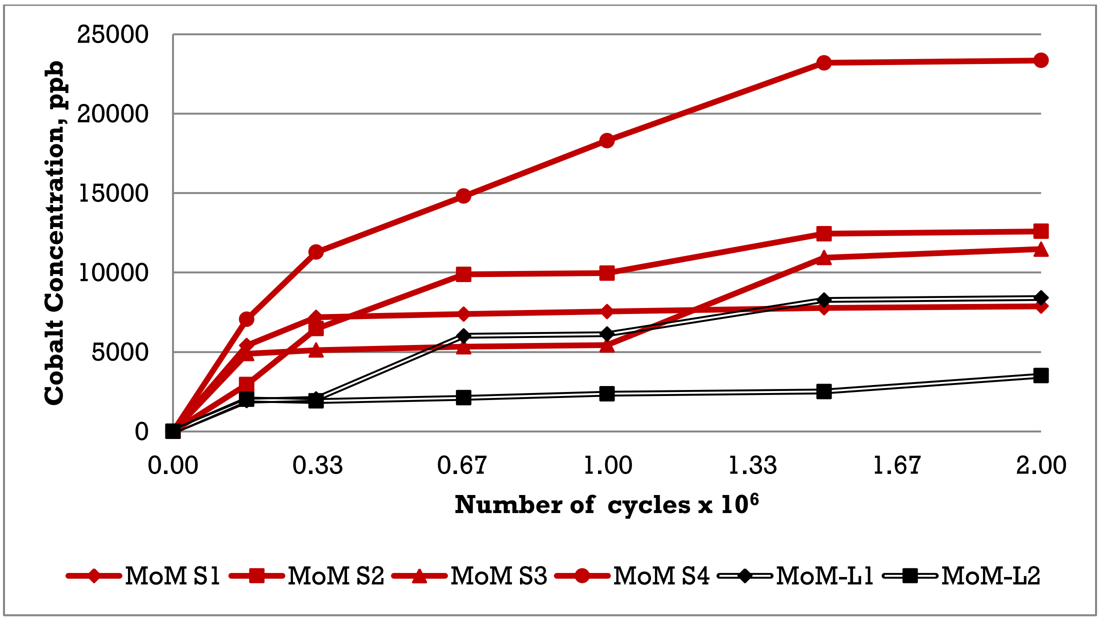

Figure 5:9: Cumulative cobalt released into test fluid over 2 mc of testing showing greater levels released under standard compared to the removed swing phase load conditions

The majority of cobalt released into the test fluid was observed to be ionic, Figure 5:10. This did not significantly differ with swing phase load, with ionic cobalt amounting to 60-70% of the total cobalt reported.

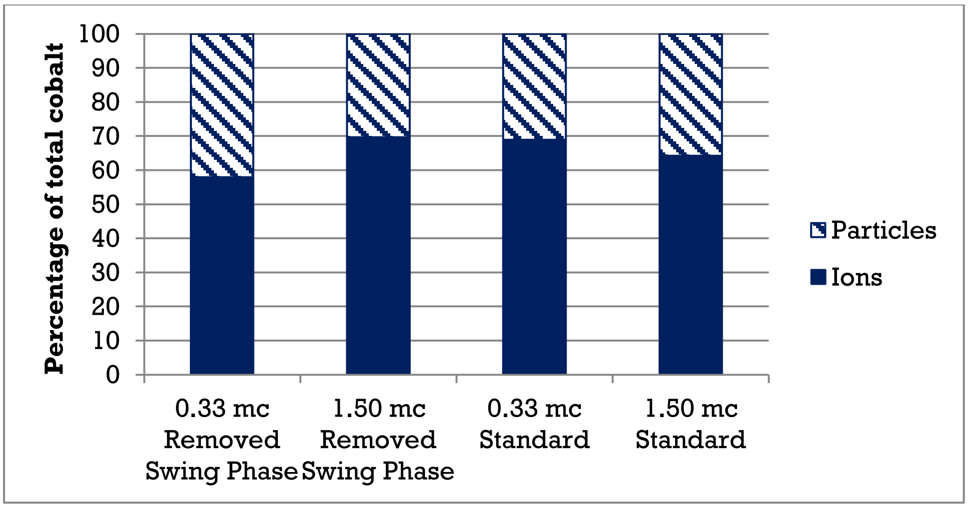

Figure 5:10: Proportion of ionic cobalt in total cobalt measured at run-in and steady state of standard and removed swing phase load conditions metal-on-metal bearings

Cobalt was measured over the first 86,400 cycles (24 hours) of testing showing 4,291.7 ± 787.3 ppb of cobalt released under standard conditions and 1,431.0 ± 29.0 ppb released with the removal of swing phase. This represented 31 and 24% of the total cobalt released over 2 million cycles respectively, Figure 5:11, suggesting the greater levels of cobalt were released during the beginning of testing under both conditions.

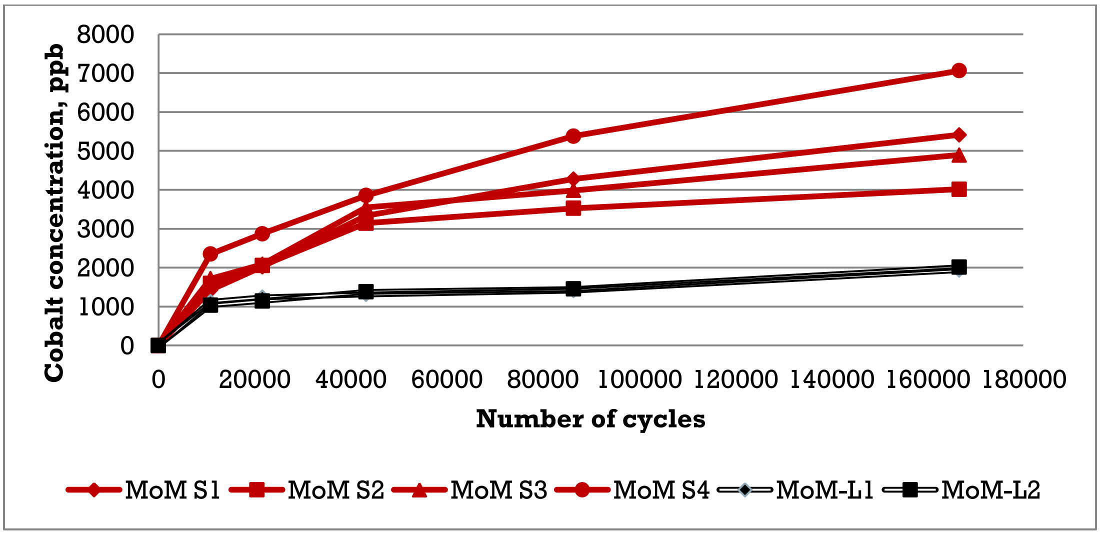

Figure 5:11: Cobalt released over the initial 24 hours of testing in metal-on-metal bearings under standard and removed swing phase load conditions

The relationship of wear and total cobalt released was found to be linear with a Pearson's correlation of 0.86 for wear and cobalt from the combined standard and removed swing phase load conditions, Figure 5:12. This correlation was stronger considering only the standard test conditions resulting in Pearson correlation's of 0.97 suggesting there may have been a difference in the relationship between wear and cobalt release between the different test conditions.

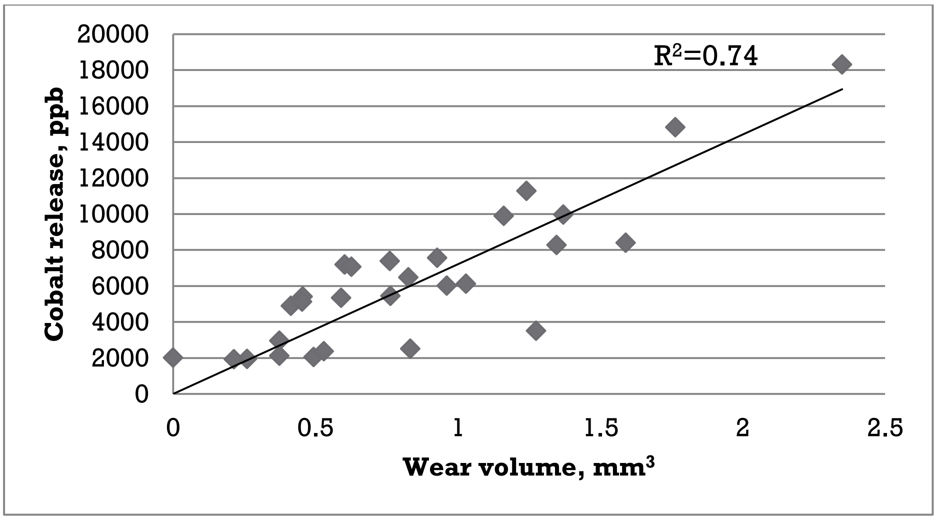

Figure 5:12: Linear relationship between wear and cobalt released in metal-on-metal bearings under standard and removed swing phase load conditions

The bearings with swing phase load removed were tested further to 4 and 5 million cycles. One bearing (MoM-L2) was stopped at 4 million cycles as dry contact between the head and cup occurred. The wear rate increased in both bearings to 0.85 ± 0.61 mm^3/mc, Figure 5:13, which was predominantly due to the increased wear of one bearing (MoM-L1) after 3 million cycles. Over the 5 million cycles of testing, the proportion of wear between the head and cup did not change from that observed at 2 million cycles.

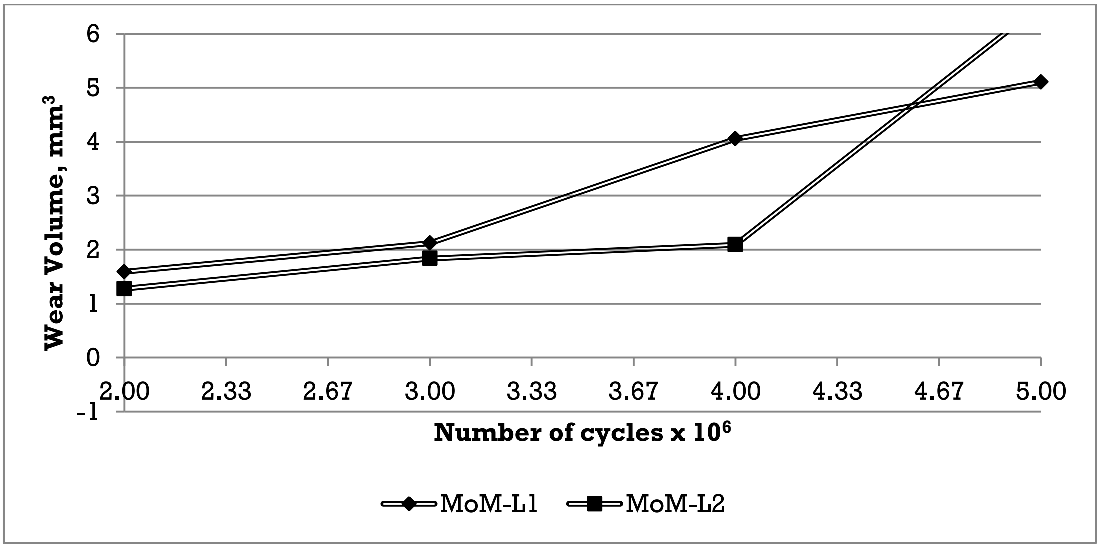

Figure 5:13: Increasing wear of metal-on-metal bearings with swing phase removed between 2 and 5 million cycles

Increasing damage was observed at the rim of the cups, Figure 5:14. The wear patch in the cup moved closer to the edge and wear in one bearing (MoM-L1) was high in the cup (3.13 mm^3 from 2 to 5 million cycles).

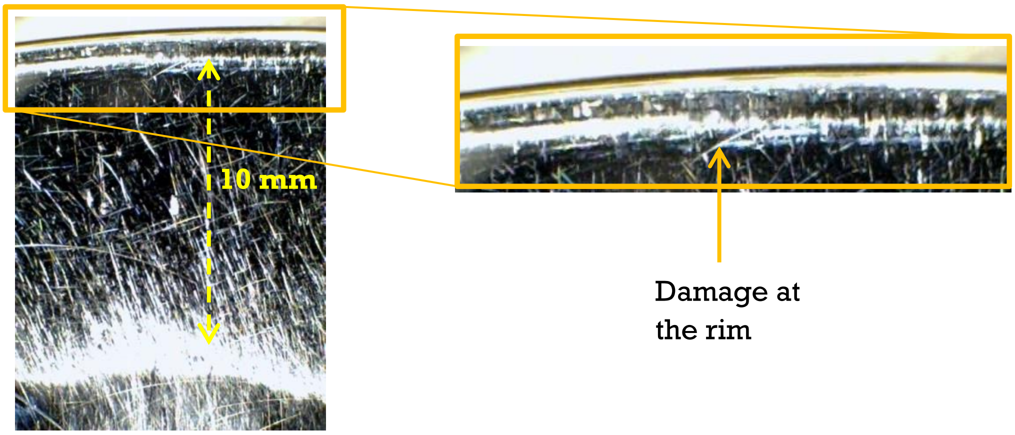

Figure 5:14: Cup rim after 5 million cycles of testing with the swing phase load removed showing increased rim damage

The rim contact between the head and cup also resulted in additional damage to the heads, Figure 5:15. Scanning electron microscopy images showed directional scratching on the side of the head generating a small wear stripe observed after 5 million cycles of testing. The wear of these heads also increased from 0.2 and 0.3 mm^3 over the first 2 million cycles to 0.4 and 0.5 mm^3 in the next 2 million cycles in MoM-L1 and MoM-L2 respectively.

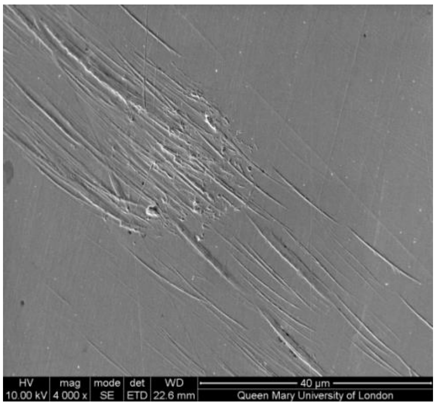

Figure 5:15: SEM image of the head showing rim contact (stripe) damage with the removal of swing phase

Cobalt continued to be released in the bearings, Figure 5:16a, following a similar trend to wear. This maintained a strong correlation (Pearson's 0.98) to the wear reported over this duration, Figure 5:16b. However, this correlation suggested that lower amounts of cobalt were released from the same amount of wear compared to at 2 million cycles, Figure 5:12. This appeared to be due to the standard wear conditions producing greater levels of cobalt than the swing phase load removed bearings, possibly as the result of the constant contact between the head and cup.

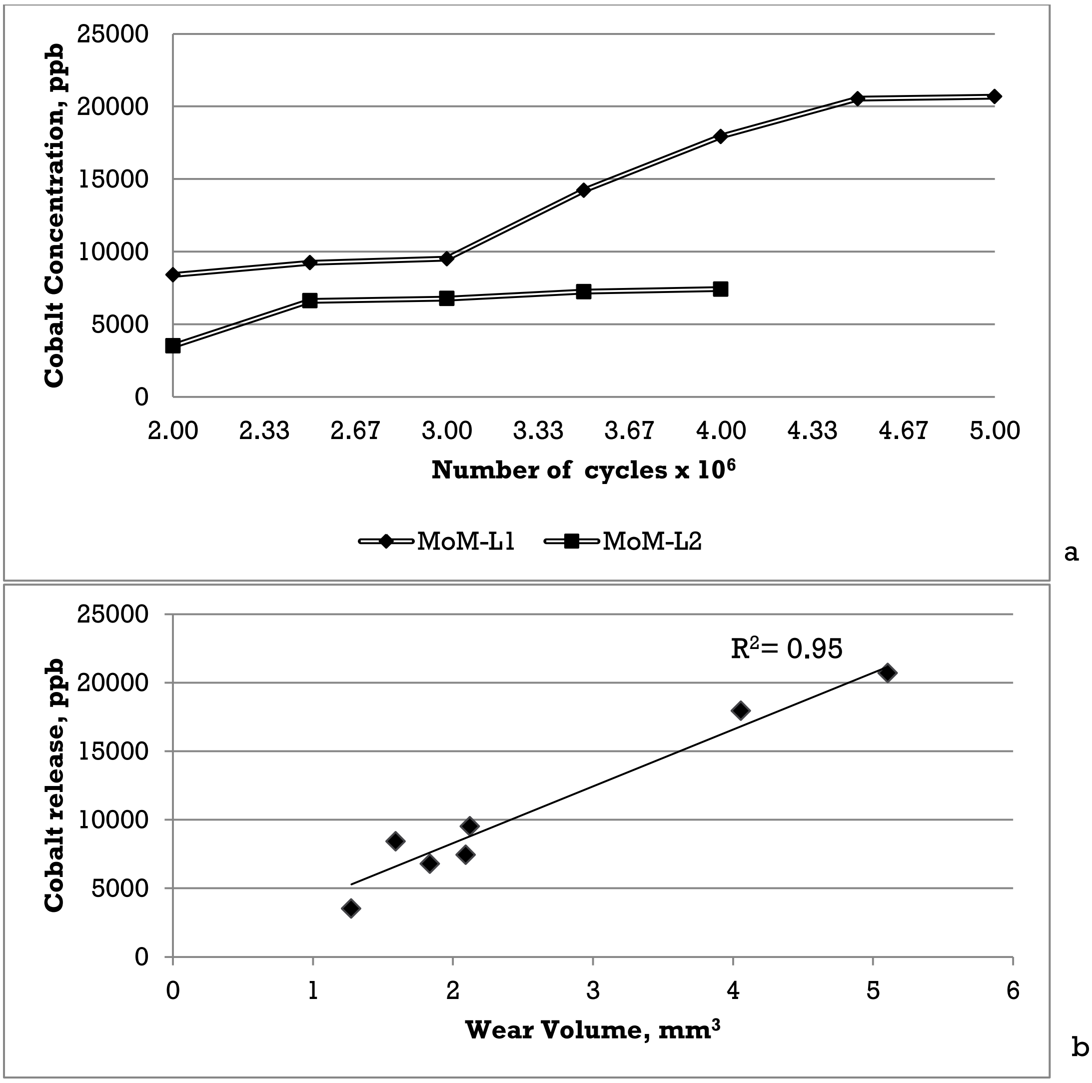

Figure 5:16: Cobalt released a) cumulatively and b) in correlation with wear reported between 2 and 5 million cycles in metal-on-metal bearings tested with the swing phase load removed

5.3.2 CrN-Ag Coatings under standard conditions

The silver rich bearings (CrN-Ag+) exhibited exceptionally high wear in the first 0.17 mc, Figure 5:17, which was visible in the test lubricant which immediately darkened during testing. Deep scratching was then observed in and around the wear patches of both the heads and cups indicating the presence of hard contaminants between the bearings although none were identified. The difference in damage resulted in varying levels of wear dependent on the amount of damage observed.

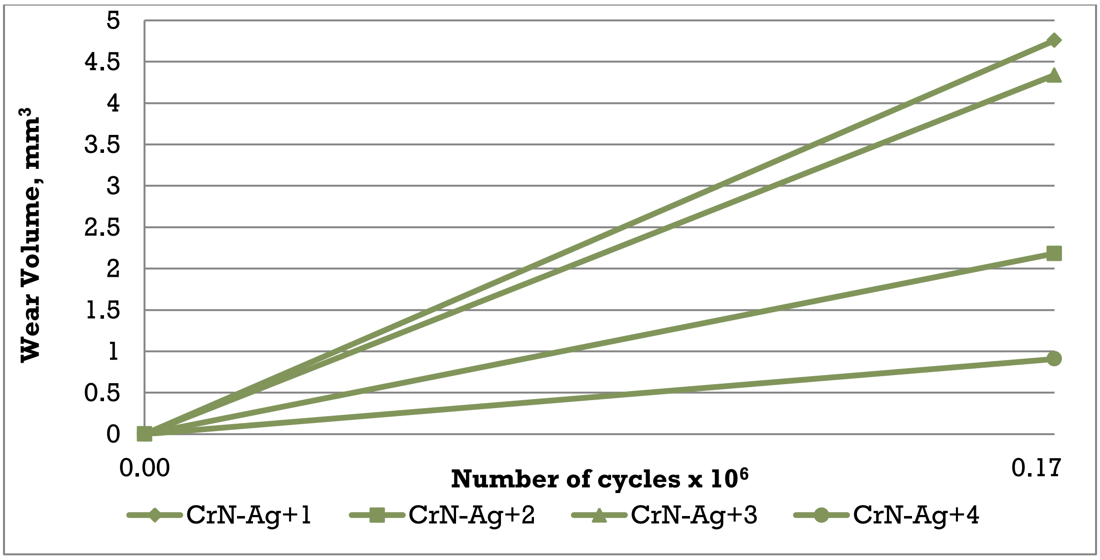

Figure 5:17: Gravimetric volume loss of silver rich chromium nitride coatings following 0.17 mc of standard testing with elevated wear due to the presence of a contaminant

The bearing showing the most damage and consequently the highest wear (CrN-Ag+1) exhibited scouring within the cup wear patch, Figure 5:18. This damage was observed in approximately a third of the total area of this wear patch. Scouring damage was also observed on the head with multiple circular scratches suggesting the contaminant was not bound to either the head or cup and instead may have circulated with the test fluid creating multiple areas of damage.

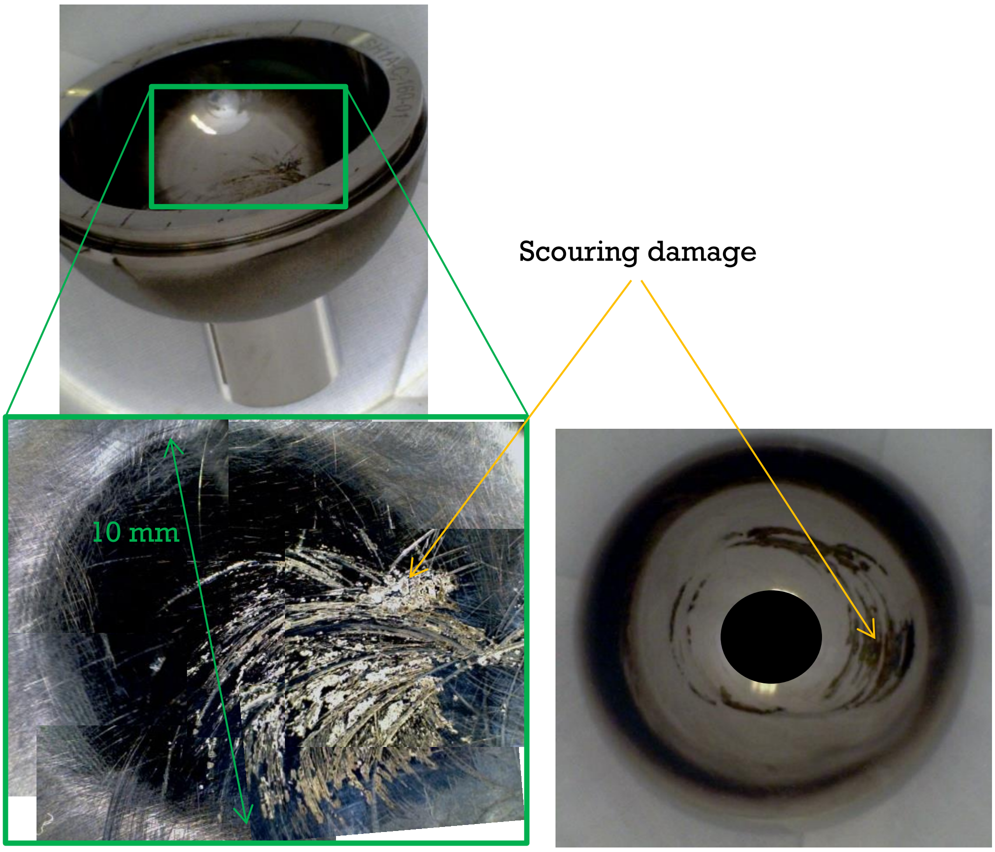

Figure 5:18: The most severe cup and head damage after 0.17 mc of testing in silver rich chromium nitride coatings

In contrast, the lowest wearing bearing couple (CrN-Ag+4) showed a cup wear patch with only a small amount of damage, Figure 5:19. A deep circular scratching tract was observed on the head but unlike the more damaged head, this remained a single scratch path. Scanning electron microscope images of this head showed areas of coating removal and, in some instances, this removal occurred to the substrate with cobalt peaks identified through energy dispersive x-ray spectroscopy. This showed small amounts of adhesive failure in which sheet-like debris was removed from the coating surface.

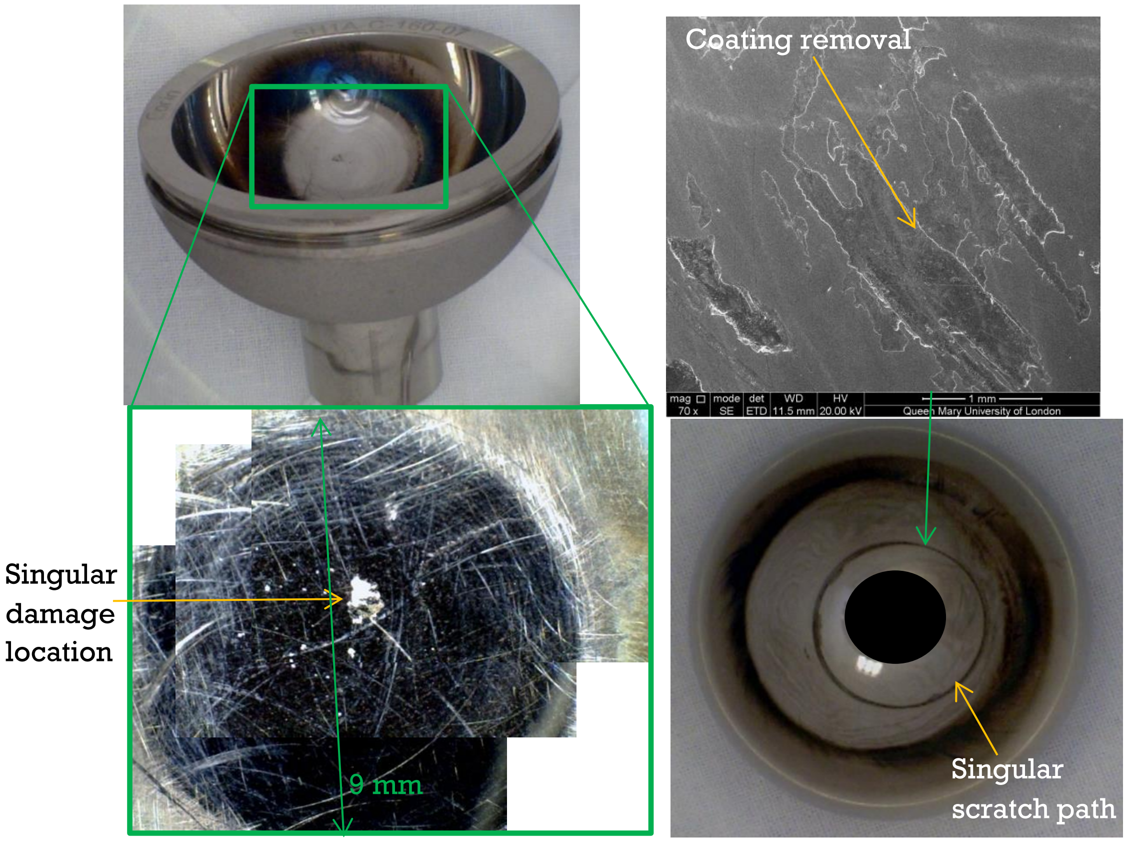

Figure 5:19: Silver rich CrN head and cup showing the least damage due to contaminant after 0.17 mc

The bearings with more overall damage showed greater proportion of head wear, despite damage being observed in both the head and the cup. In the lower wearing bearing which showed minimal damage, 36% of the total wear resulted from head wear yet this substantially increased to 53% in the highest wear bearing, Figure 5:20. The relationship between proportion of head wear and the total wear was observed as linear with a Pearson's correlation of 0.99.

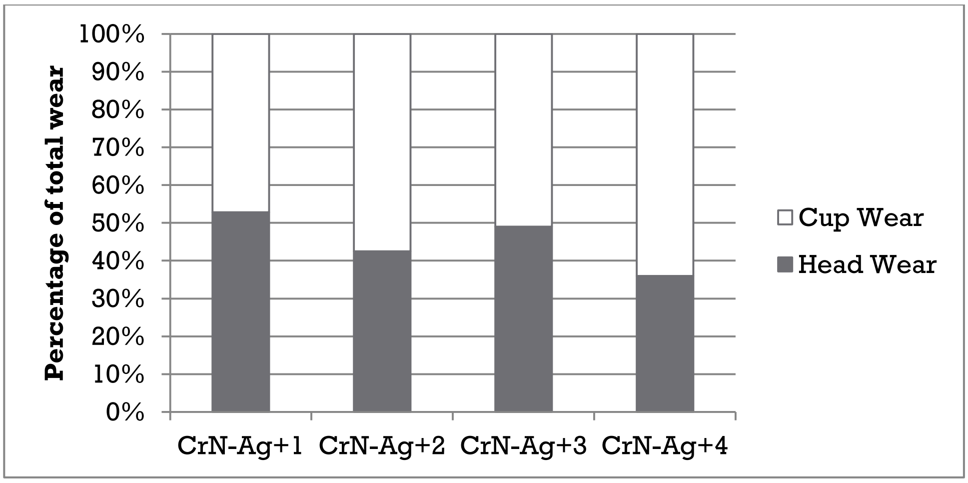

Figure 5:20: Proportion of head and cup wear in the silver rich CrN bearings with the majority of wear generated from the cup

Despite the increased wear and observed damage of the coating, the cobalt release remained very low (below 50 ppb) Figure 5:21. The indication is therefore that the damage observed did not remove all the coating, possibly retaining at least the chromium adhesion layer in the majority of the damaged area as this was harder than the silver chromium nitride coating and may have withstood damage.

Silver release from the coatings was significant, with a mean concentration of 6,380 ± 2230 ppb, representing the removal of the silver chromium nitride coating although no relationship was observed between silver release and wear.

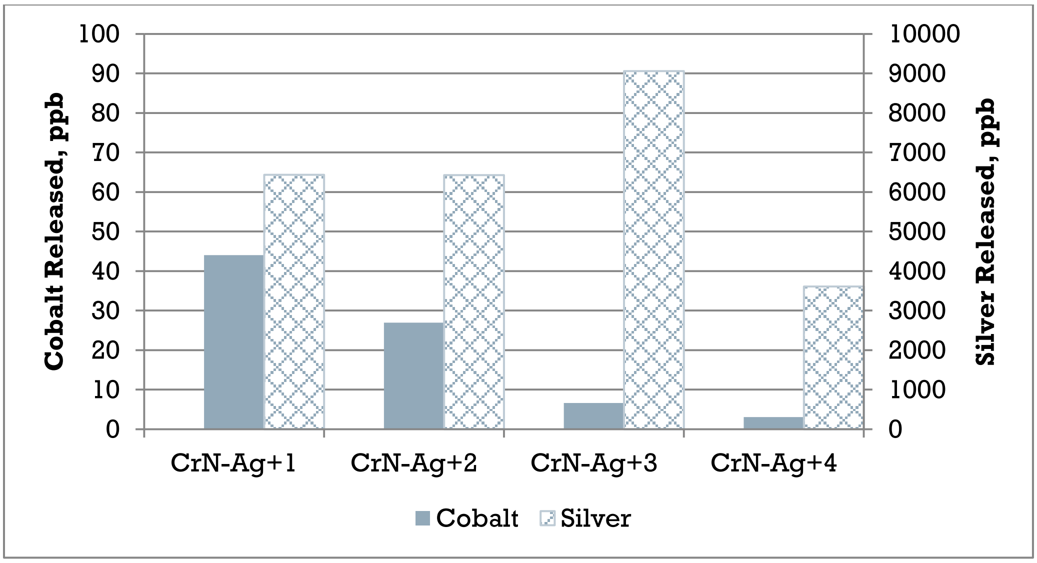

Figure 5:21: Cobalt and silver released from the silver rich CrN coatings during 0.17 mc in which the coatings were damaged

The three highest wearing silver rich CrN cups were remounted on the hip simulator after full cleaning in a different orientation to allow testing on unworn areas and paired with the damaged heads. This test showed a different wear performance, Figure 5:22, comparable to the wear of the lowest wear silver rich CrN bearing in the initial 0.17 mc. Silver depleted surface CrN coatings which had been tested for 5 million cycles under lateralised conditions were remounted in a similar manner as the silver rich CrN coatings and showed lower wear than these bearings.

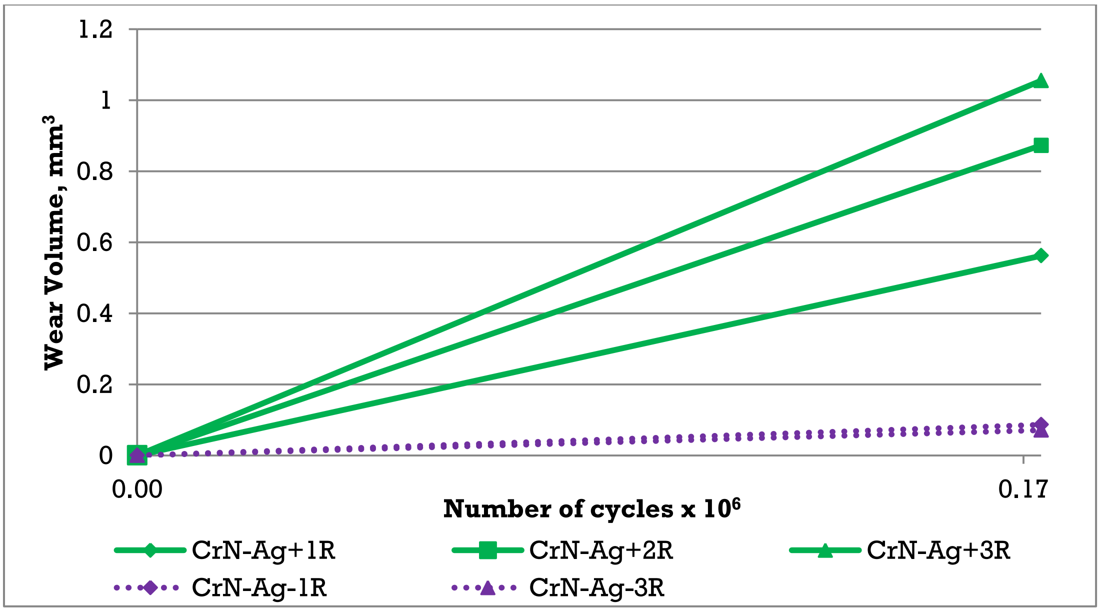

Figure 5:22: Gravimetric wear of silver rich and depleted CrN coatings with the cup remounted in a different position for 0.17 mc

Despite the reduction in wear with the rotation of the cups, the wear rate (run-in) was still high in the silver rich coating but significantly ($p<0.05$) decreased from the pristine bearings which has been damaged, Table 5:3. The increased wear rates from the silver rich CrN bearings compared to the silver depleted CrN bearings were significant ($p<0.05$) and possibly due to the increased silver content which resulted in a softer coating than the CrN surface coating. As well as this, damage in the heads could not be removed and therefore may have elevated the wear rates.

Table 5:3: Run-in (0-0.17 mc) wear rates of silver doped CrN coated metal-on-metal bearings

Bearings	**Number of bearings**	**Wear rate, mm^3/mc**
Silver rich surface CrN	4	22.69 ± 13.54
Silver rich CrN rotated	3	5.24 ± 1.57
Silver depleted CrN rotated	2	0.46 ± 0.06

No further progression of damage was observed in the silver rich bearings. The heads maintained the scratches observed in the initial 0.17 mc and wear patches on the cups showed no scouring damage, Figure 5:23. The wear patch showed light and dark banding signifying the removal of different layers of the coating suggesting nanolayering of the coating.

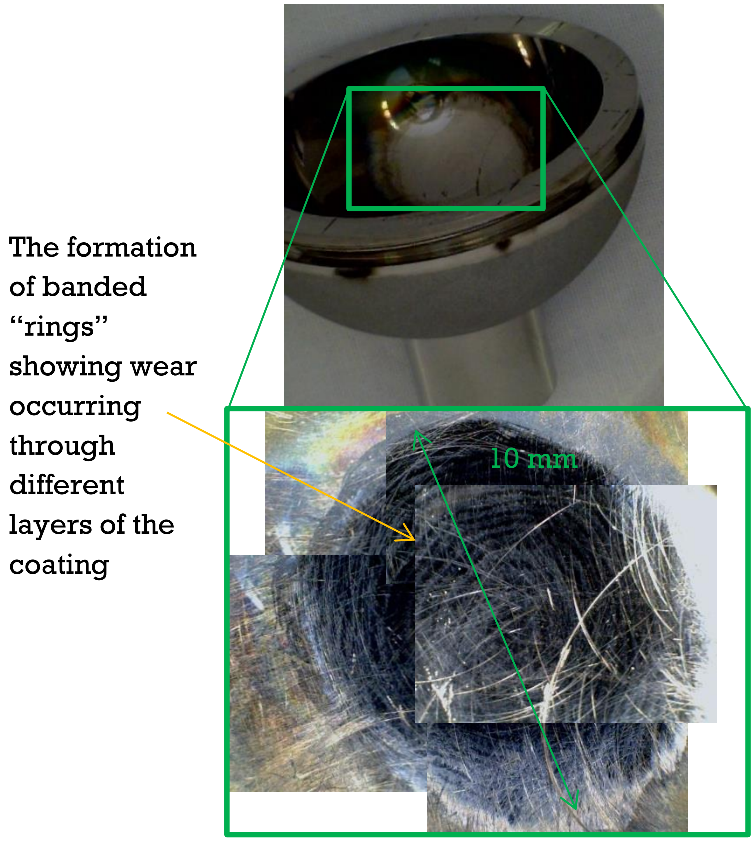

Figure 5:23: Silver rich CrN head and cup showing no damage progression with the rotation of the cup and 0.17 mc of further testing

The silver depleted CrN cups produced a small wear patch on the rotated portion of the cup, Figure 5:24. This did not show the same layering as the silver rich chromium nitride wear patches, presumably due to the lack of silver at the surface and lower wear.

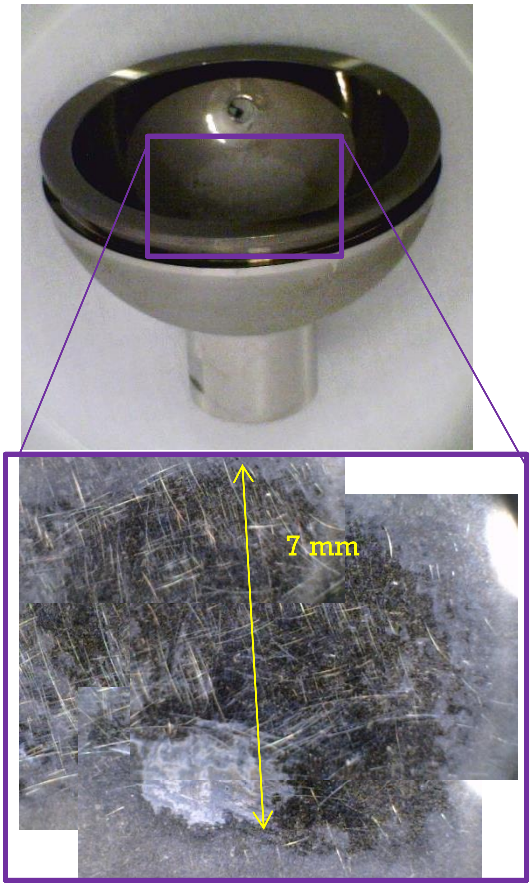

Figure 5:24: Silver depleted surface chromium nitride coating after 0.17 mc with the cup rotated

The proportion of head wear decreased in the silver rich CrN coatings, Figure 5:25. This maintained a linear relationship (Pearson's correlation of 1) between percentage head wear and total wear with increasing head wear relating to increased total wear. The highest wearing bearing produced roughly 39% of wear from the head, a similar to the percentage to CrN-Ag+4 in the original state and produced a similar amount of wear (1.06 mm^3 compared to 0.91 mm^3). The silver depleted CrN coatings did not exhibit this relationship, with the lower wearing bearing producing a greater (28%) of wear from the head.

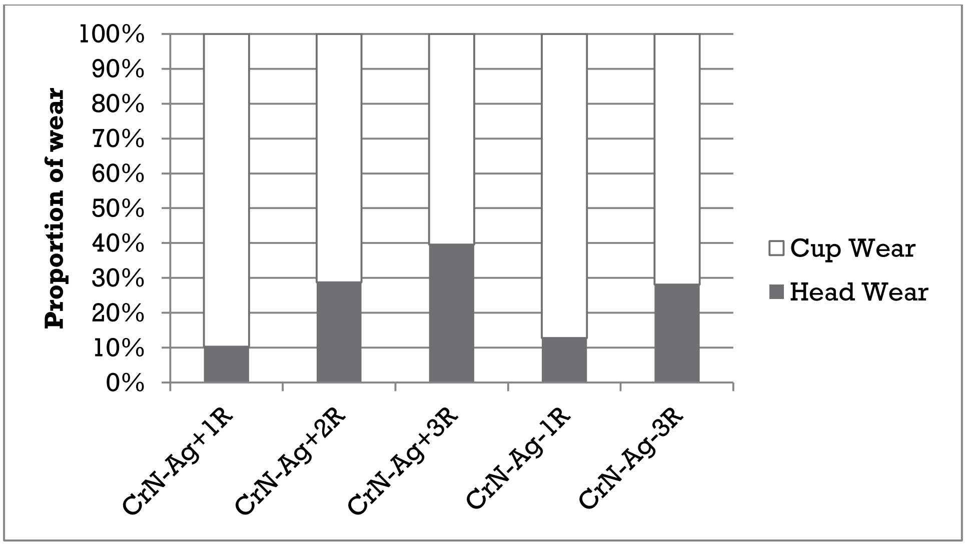

Figure 5:25: Proportion of head and cup wear in the silver CrN bearings after cup rotation and 0.17 mc of standard testing

All bearings generated negligible cobalt, below the level of detection (<5 ppb). The silver rich coatings produced significantly ($p<0.01$) greater levels of silver, with a mean concentration of 3,720 ± 360 ppb, compared to the silver depleted coatings (140 ± 50ppb), Figure 5:26. A linear relationship (Pearson's correlation of 0.94) was established between silver released and wear.

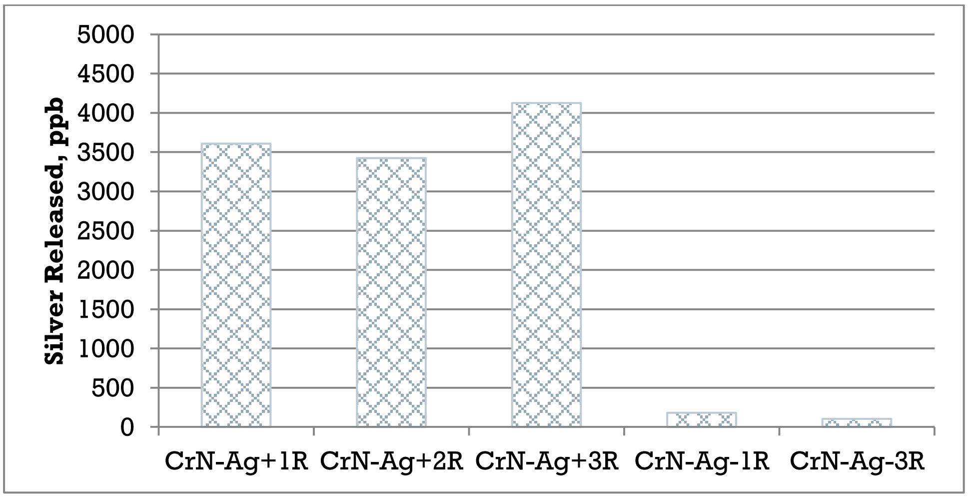

Figure 5:26: Silver released by the silver doped CrN coated bearings after 0.17 mc of standard testing in a rotated position showing increased silver release with increased silver surface concentration

Spinning of the fluid revealed the silver produced in both coatings to be in particulate form (over 99% of the total silver measured). These particles were noticeably different in appearance to those observed from the CoCrMo alloy metal-on-metal tests, Figure 5:27. The particles were between 1 and 500 nanometres in size, Figure 5:28. Although the majority of particles produced were less than 20 nm in size, the particles produced from the silver depleted coating were larger with a mode of 18 nm compared to 13 nm in the silver rich CrN bearings. The silver depleted CrN coatings also generated greater amounts of particles sized between 100-500 nm.

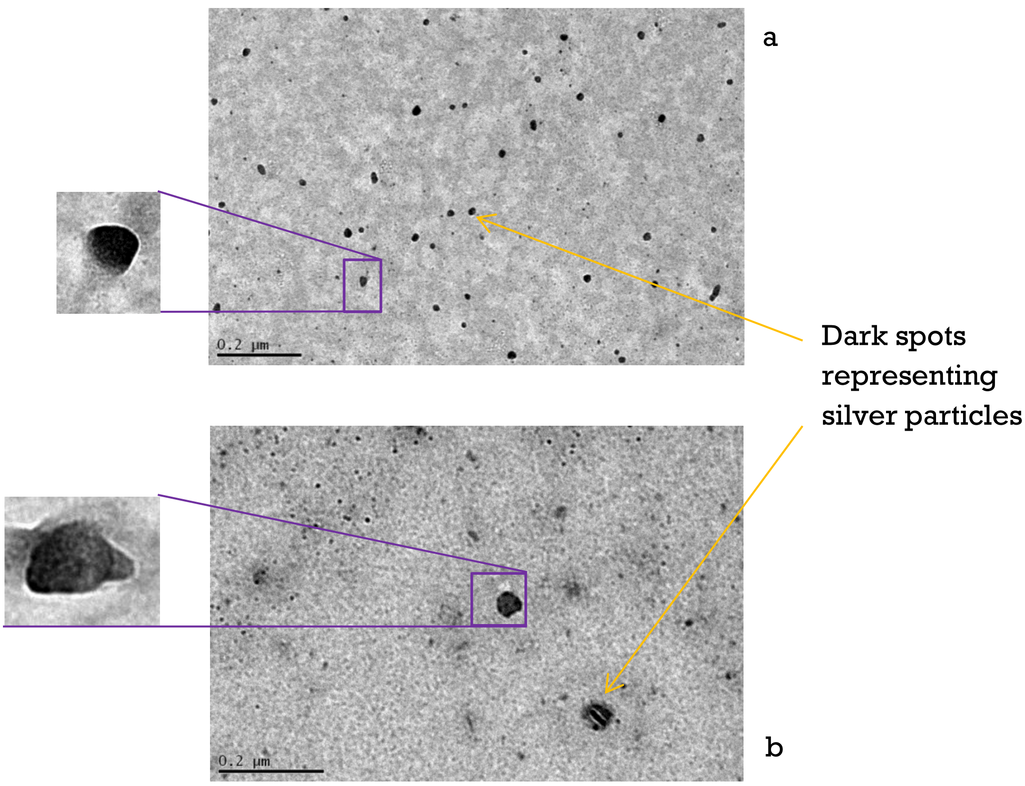

Figure 5:27: Transmission electron microscopy images of particles produced (a) from silver rich chromium nitride and (b) silver depleted chromium nitride coatings

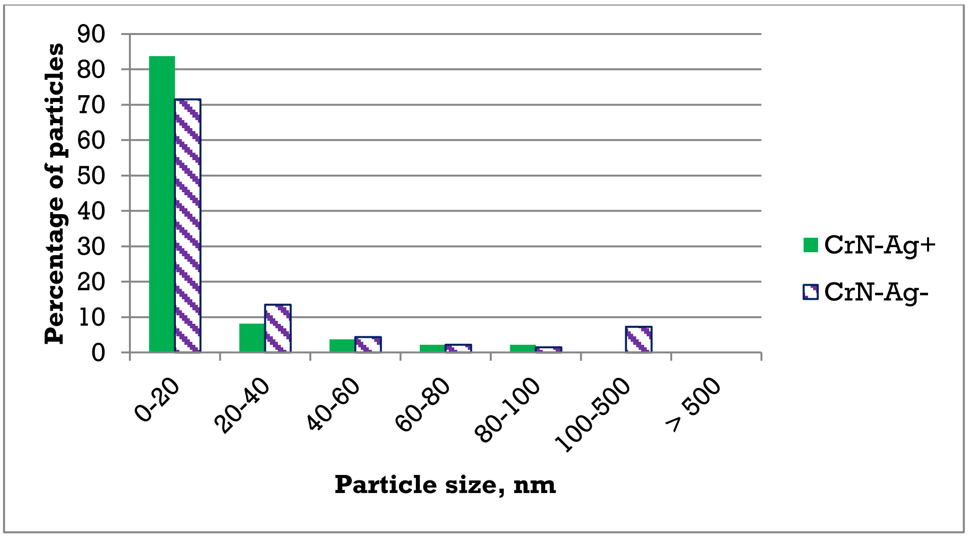

Figure 5:28: Wear particle distributions generated from silver chromium nitride coatings showing similar distributions

5.3.3 Lateralisation conditions in coated and uncoated metal-on-metal

The introduction of lateralisation increased the wear rate in both the low surface silver CrN-Ag coated and uncoated metal-on-metal bearings, Figure 5:29. The wear of the uncoated bearings was, overall, higher than the coated bearings overall, but not statistically significant ($p>0.05$).

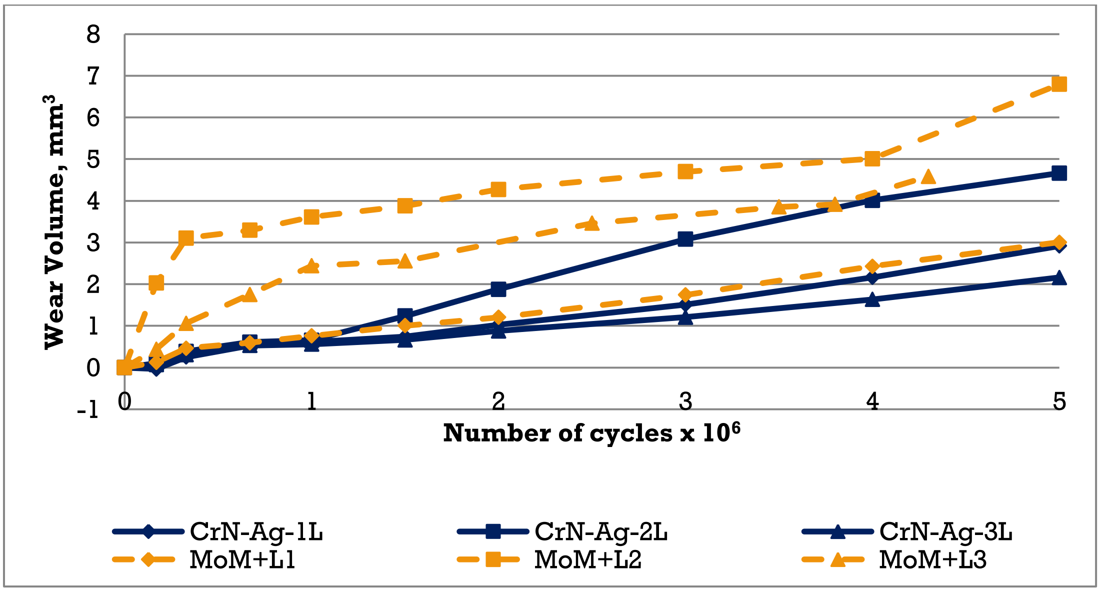

Figure 5:29: Gravimetric wear of metal-on-metal and CrN-Ag coated bearings with decreased silver surface content under lateralisation conditions

The metal-on-metal bearings displayed a bi-phasic wear pattern with an initial high run-in period (0-1.00 million cycles) followed by a lower steady state phase (after 1 million cycles). The wear rate during this extended run-in was not significantly ($p>0.05$) increased from the standard run-in wear rate as reported in section 5.3.1. The steady state wear rate was elevated although also not significant ($p>0.05$), due to variation in the wear of the lateralised bearings. The lateralised silver depleted CrN coating maintained a consistent wear rate throughout testing at 0.65 ± 0.30 mm^3/mc, Table 5:4. This lateralisation wear rate was significantly ($p<0.05$) higher than the rotated bearings of similar silver content under standard conditions in section 5.3.2 but significantly ($p<0.01$) lower than the bearings with increased silver concentration at the surface. The silver depleted CrN coating reduced the run-in wear ($p<0.05$) in the lateralised bearings compared to the uncoated metal but there was no significant difference ($p>0.05$) in the steady state wear rates.

Table 5:4: Mean run-in (0-1 mc) and steady state (1-5 mc) wear rates of metal-on-metal and silver chromium nitride coated bearings under lateralisation

Bearing	Number	Wear rate, mm^3/mc	
		Run-in	Steady state
MoM	3	2.07 ± 1.18	0.68 ± 0.33
Ag depleted CrN coated	3	0.67 ± 0.06	0.65 ± 0.07

The increased wear rates were observed with a change in the wear region of the heads. The separation generated in the bearings during swing phase, removed part of the elliptical wear patch on the head creating a crescent shaped wear patch, Figure 5:30. This wear area covered a greater area (25%) in the coated heads compared to the uncoated heads (21%). This small difference may be due to the greater contrast in CrN-Ag heads between the unworn and worn areas allowing wear locations to be identified with greater ease and accuracy. An additional stripe was observed on the side of the heads. This was approximately 28 mm long and 3 mm wide in the uncoated heads and 32 mm long and 2 mm wide in the coated heads. The coated heads also appeared to show some damage between the wear patch and stripe possibly generated during the relocation process.

The wear stripes produced on the heads were formed of several scratches, Figure 5:31. These scratches varied in depth from 20 to 120 μm in the metal head and 20 to 90 μm in the coated head, however these measurements were not taken perpendicular to the scratches. The coated head scratches appeared broader than those on the metal head possibly due to the scratches in the heads appearing at different angles, but the surface roughness, Ra of the heads was comparable in the coated and uncoated heads

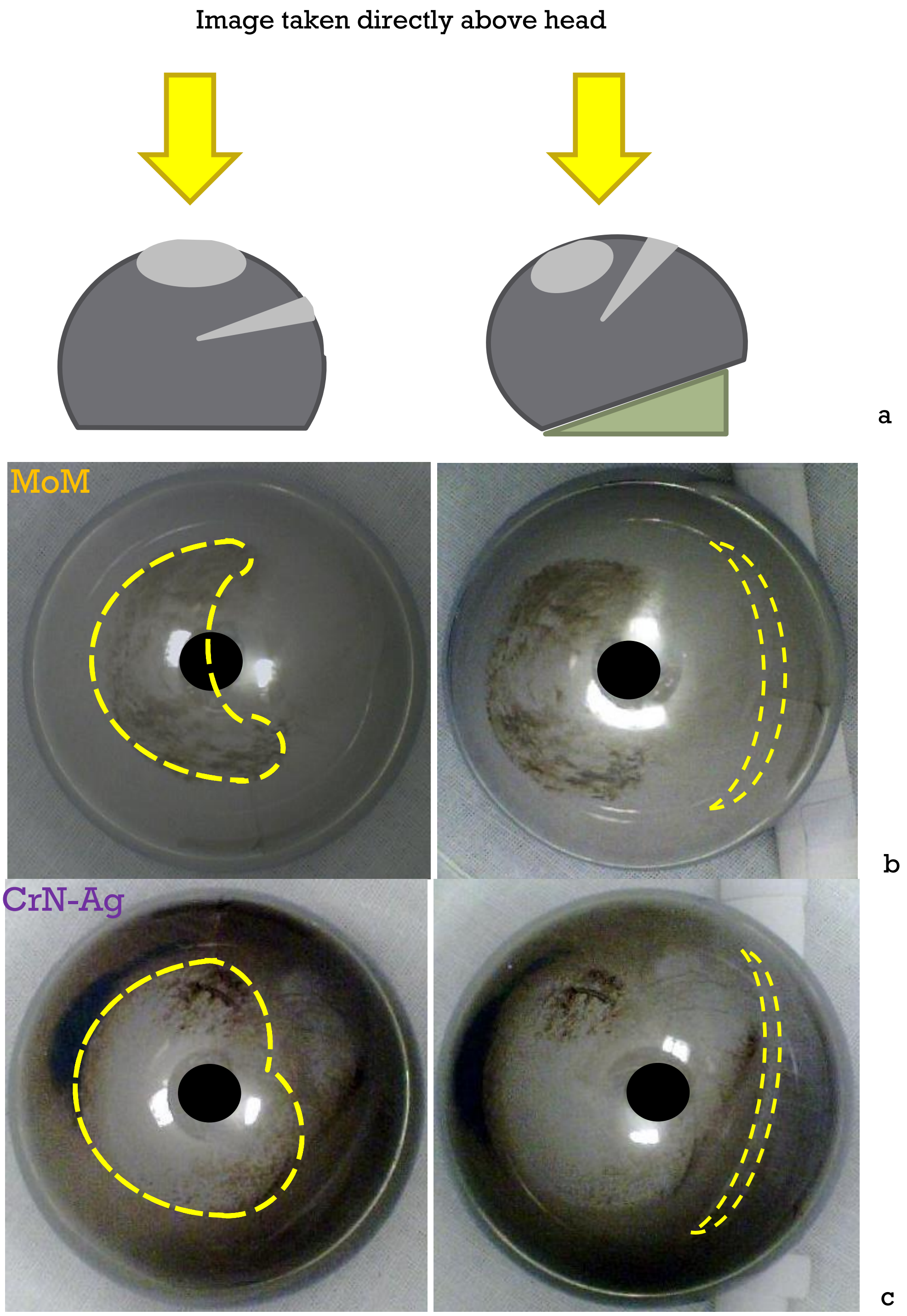

Figure 5:30:Wear patch (left) and stripe (right) imaged directly above when the head was flat and tilted (a) as shown by schematic after 5 million cycles in (b) metal and (c) CrN-Ag head (dotted lines outline the wear patches)

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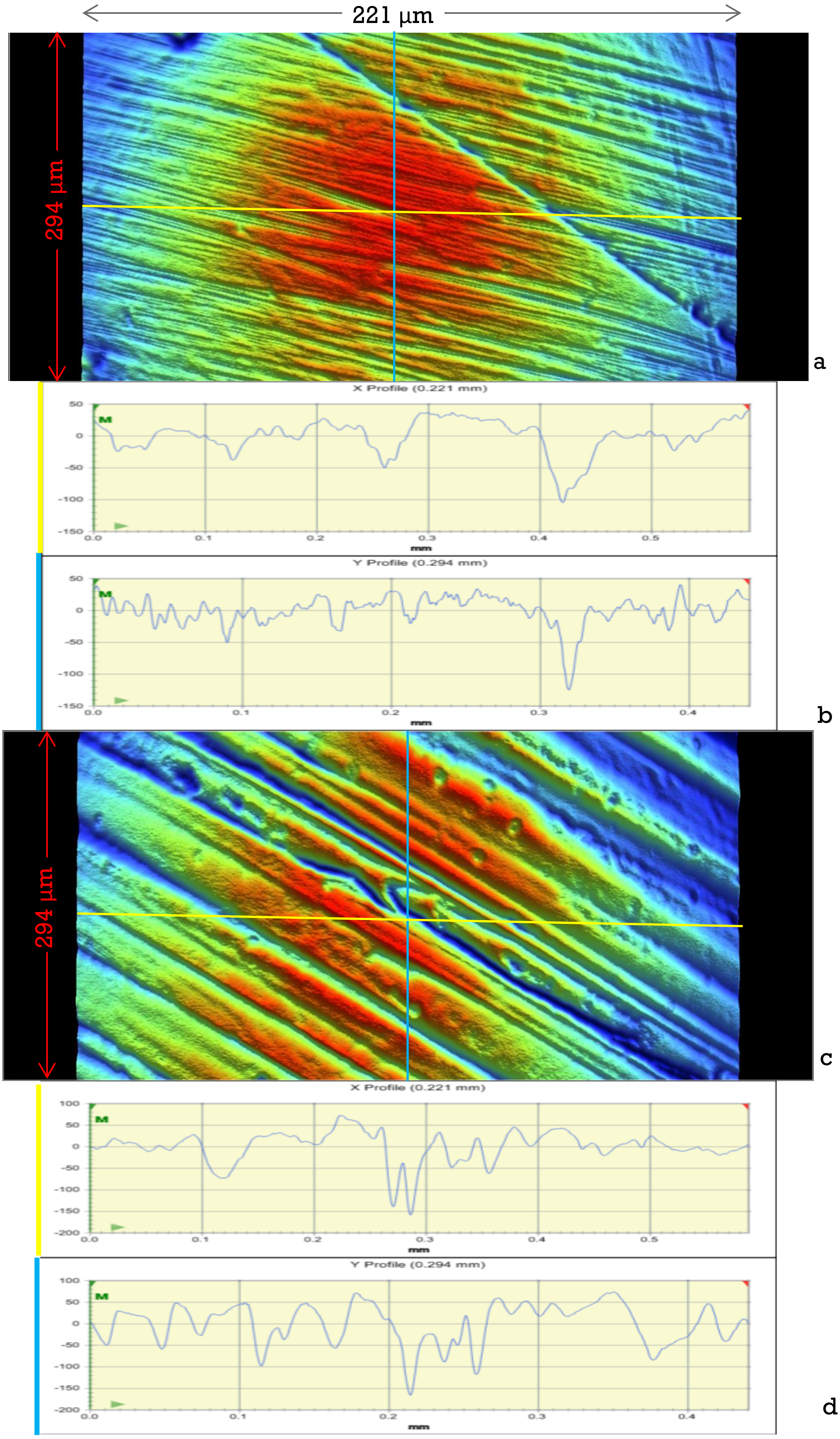


Figure 5:31: Optical surface profilometer images of the wear stripes in (a) metal and (c) CrN-Ag coated heads and (b,d) the surface profiles of these scratches

The generation of wear stripes on the heads was paired with the rim damage on the cups, Figure 5:32. The wear patch on the cups was similar to that of generated under standard wear conditions and was separate to the rim damage observed. In the uncoated metal cups, this rim damage appeared greater than in the coated cups.

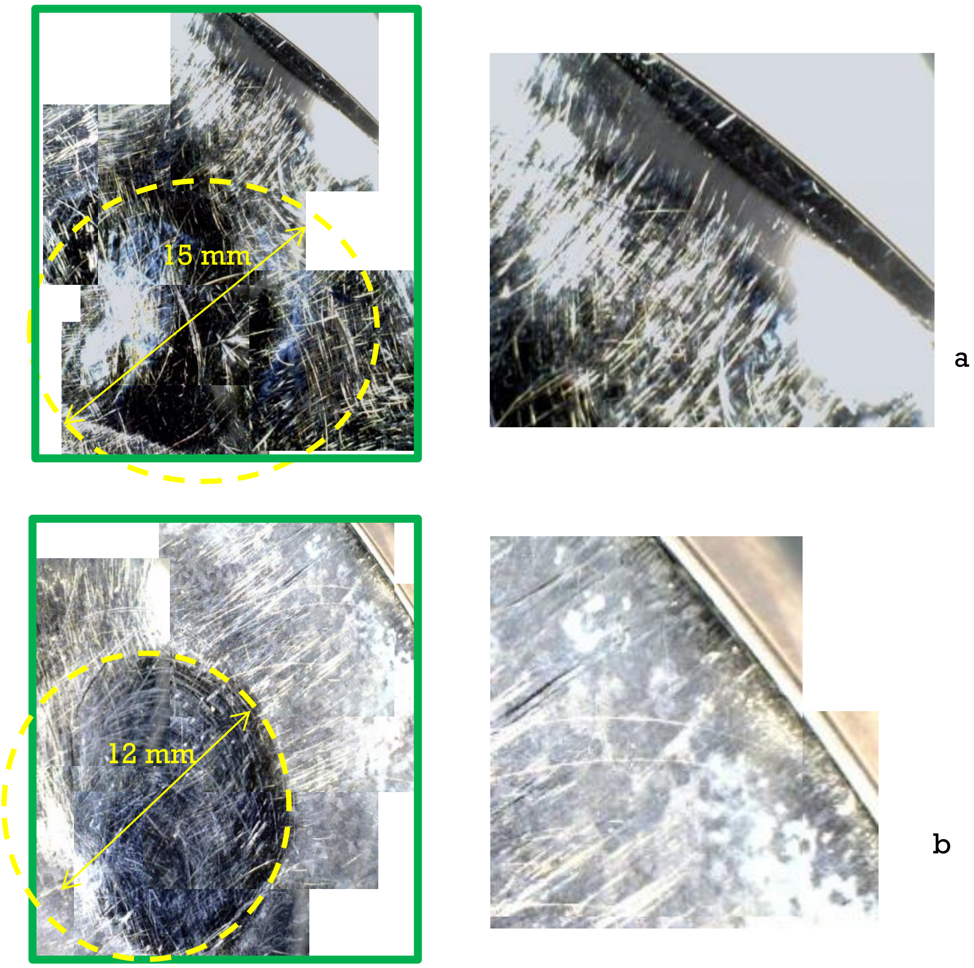


Figure 5:32: Wear patch (dotted outline) and additional rim contact in (a) metal and (b) CrN-Ag coated cups

The majority of wear occurred on the cups of the components and the metal-on-metal bearings showed the same linear correlation (Pearson's correlation 0.96) with increasing proportion of head wear resulting in increasing overall wear. After 5 million cycles, the proportion of head wear was 23-35% with two of three bearings showing consistent head wear between 31 and 39 % over the duration of testing, Figure 5:33. The other metal-on-metal bearing (MoM+L1) and the coated bearings showed a gradual increase in the proportion of head wear. In the coated components after 5 million cycles, head wear contributed to 36-46% of total wear in the uncoated heads and 24-35% in the coated heads.

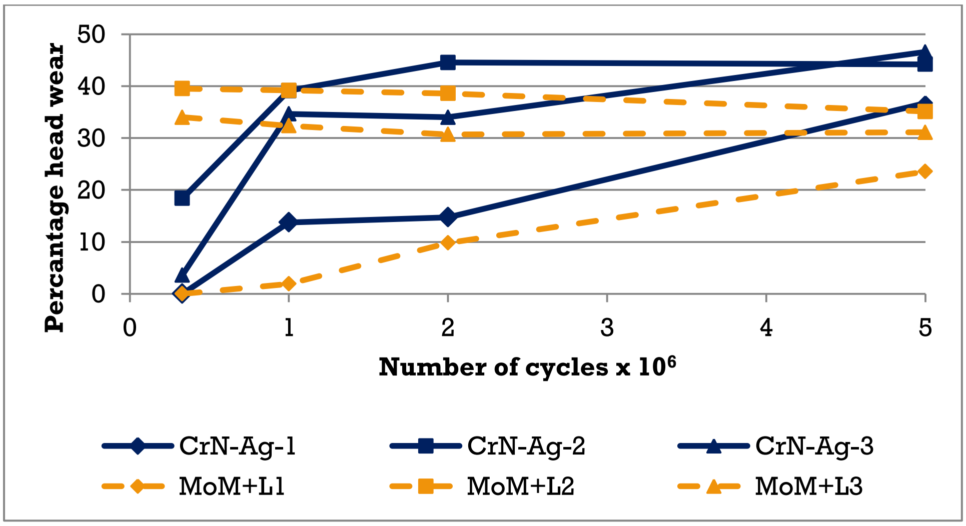
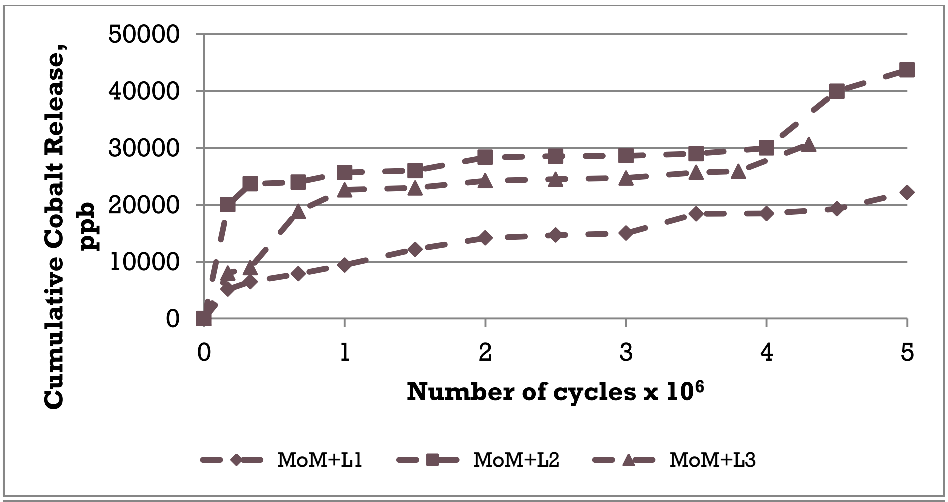
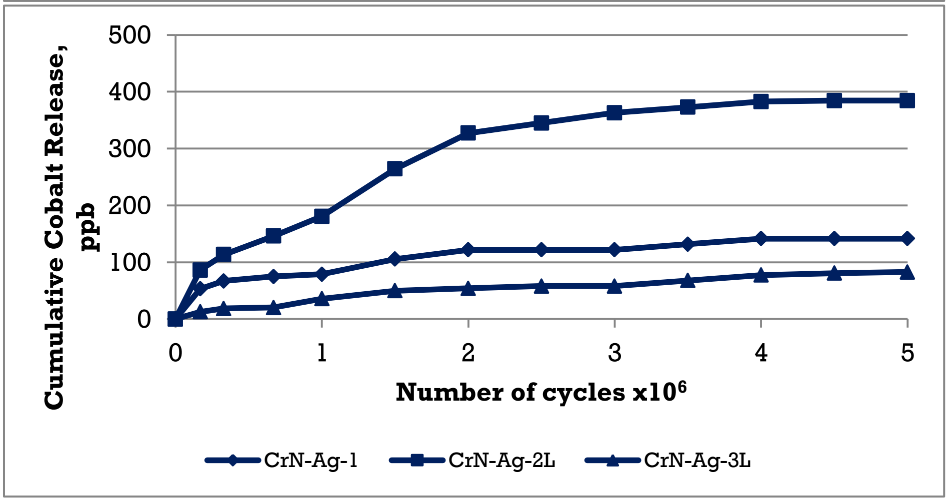


Figure 5:33: Percentage of head wear over the duration of lateralisation testing showing consistent proportion in the uncoated bearings compared to an increasing proportion of head wear in the coated bearings

Cobalt released throughout testing was measurable in both coated and uncoated bearings but was significantly ($p<0.01$) greater in the uncoated bearings, Figure 5:34. After 5 million cycles, the uncoated bearings released on average 32,157 ± 10,386 ppb while the coated bearings released 203 ± 160 ppb, two orders of magnitude less cobalt. One coated bearing (CrN-Ag-2) produced greater levels of cobalt, as observed in the gravimetric wear measurements yet showed no additional damage compared to the other coated components.



a



b

Figure 5:34: Cobalt released over 5 million cycles of lateralisation testing in (a) metal-on-metal and (b) silver chromium nitride coated bearings

Both sets of bearings produced more cobalt in the first million cycles than at any time of testing thereafter showing a similar trend in cobalt release to wear. This resulted in linear relationships between cobalt release and metal wear with a strong Pearson's correlation of 0.98, Figure 5:35. This linear relationship however, showed 5,000 ppb of cobalt released when no wear was recorded suggesting that the gravimetric methods to determine wear may have underestimated the wear. In the coated components, this relationship was not as strong, 0.79, as the cobalt release was low.

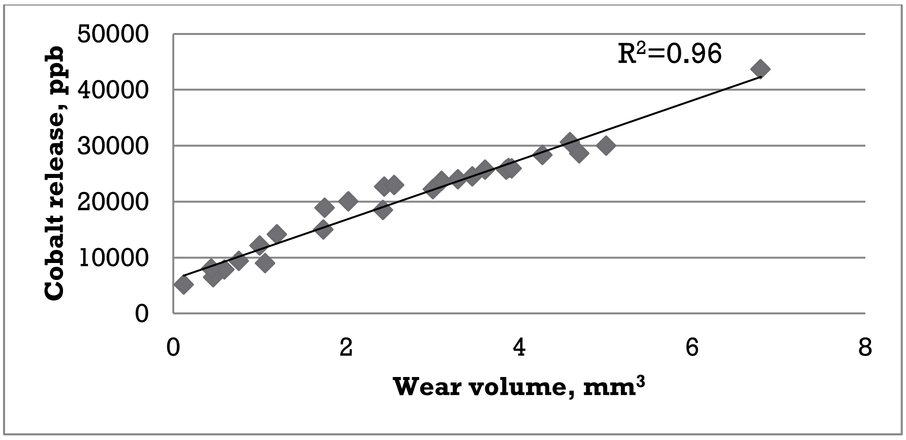


Figure 5:35: Linear relationship between wear volume and cobalt release in metal-on-metal bearings under lateralisation conditions

Of the cobalt reported, the metal-on-metal bearings consistently produced 83% ions and the remainder particles, Figure 5:36. The CrN-Ag coating released such low levels of cobalt (less than 100 ppb each time point) that it was not possible to determine the ionic percentage.

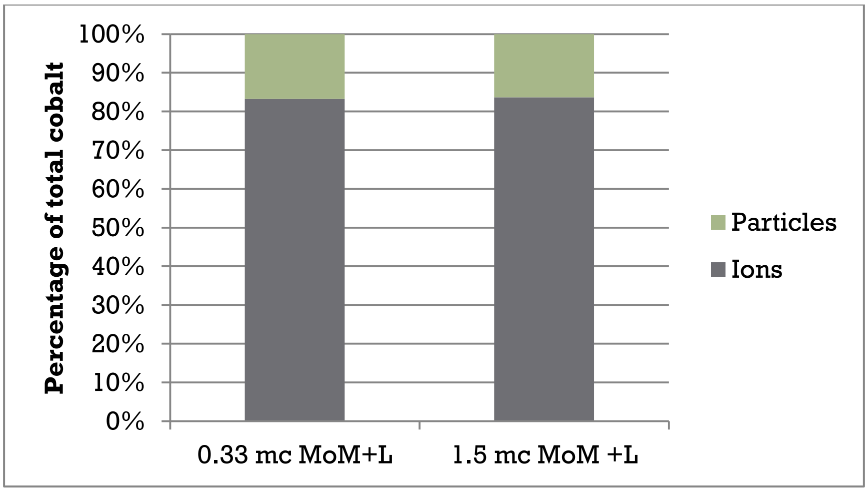


Figure 5:36: Percentage of cobalt ions and particles in total cobalt released from metal-on-metal bearings at different time points of testing

The particles produced by the metal-on-metal bearings showed similar morphology to the standard test conditions, Figure 5:37. The particles produced were also nanometre sized with a mode particle size of 15 nm, but more particles

(45%) were greater than 20 nm, Figure 5:38, compared to standard conditions (25%).

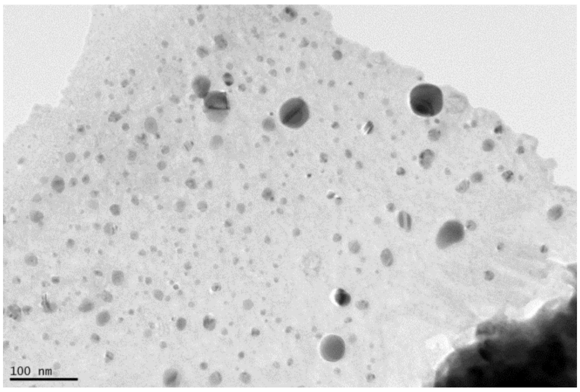


Figure 5:37: Transmissopm electron microscopy images of particles produced during metal-on-metal lateralisation testing

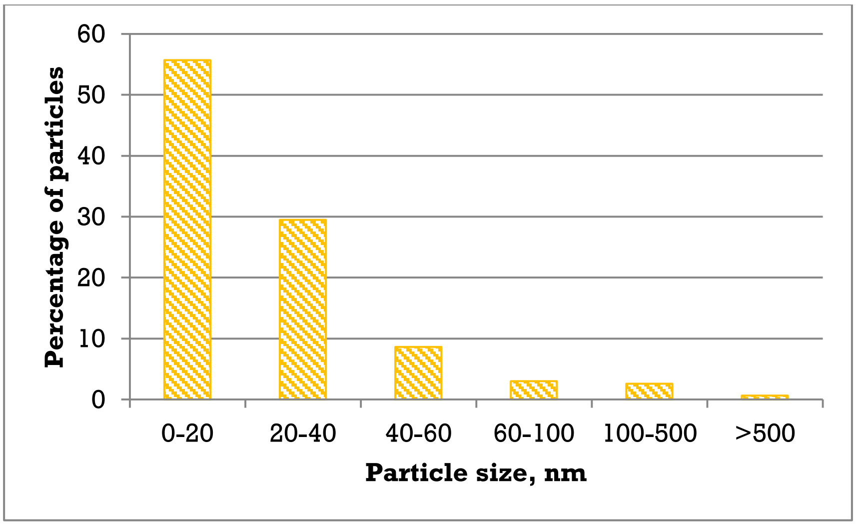


Figure 5:38: Particle distribution of those produced in metal-on-metal bearings under lateralisation conditions showing predominantly small (less than 100 nm) particles produced

While the coated components did not produce large amounts of cobalt throughout testing, silver was measurable throughout with a mean of 18,800 ± 8200 ppb produced after 5 million cycles, Figure 5:39. Over the first third of a million cycles, large amounts (mean of 2,200 ± 480 ppb) of silver were released, which reduced over the remainder of the first million cycles and remained at this low rate in two of the bearings. One bearing (CrN-Ag-2), however, showed increased silver release after one million cycles, correlating to the increased wear observed in that bearing.

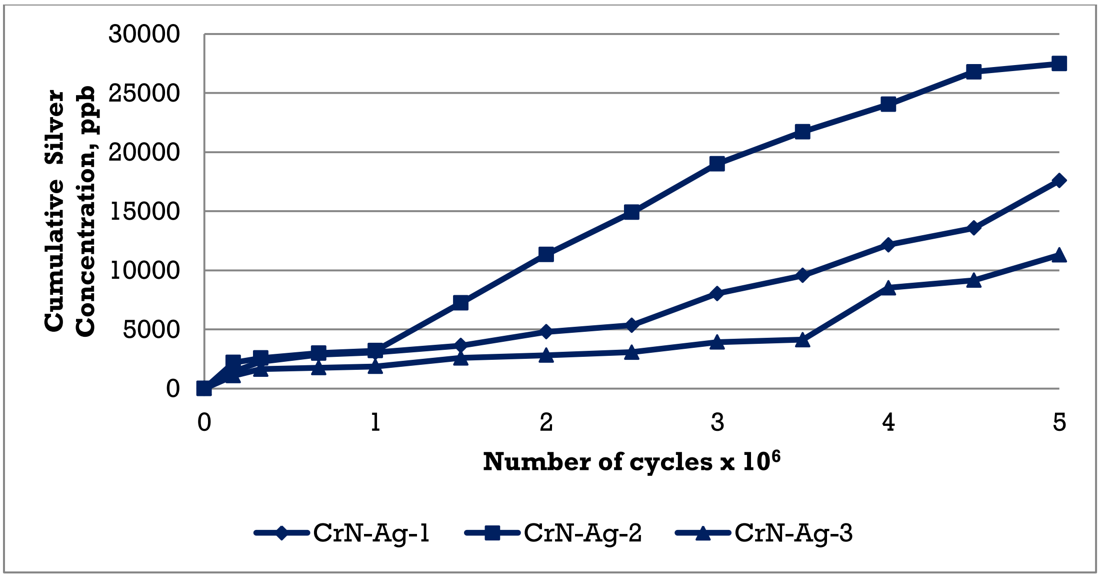


Figure 5:39: Cumulative silver released in silver chromium nitride coatings over 5 million cycles of lateralisation

As the total wear and silver release showed a similar trend, a linear relationship was observed with a Pearson's correlation of 0.99, Figure 5:40. Spinning of fluid at 0.33 and 1.5 mc revealed the majority of silver to occur in particulate form as observed under standard conditions, Figure 5:41. At 0.33 mc, over 90 % of the silver reported was particulate but the ionic percentage decreased to approximately 5% at 1.5 million cycles suggesting that less ionic silver may be released with increasing test duration possibly due to the higher concentration of silver being exposed as the low silver surface wore away.

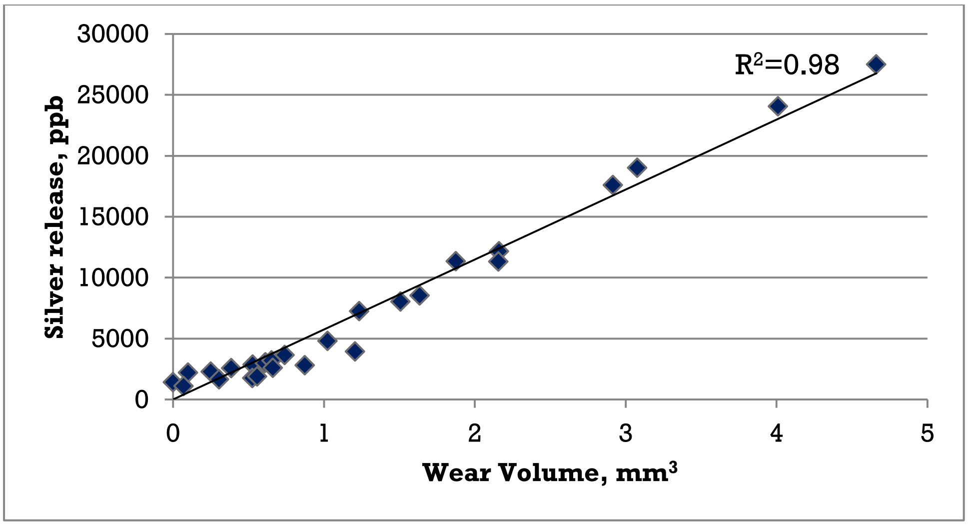


Figure 5:40: Linear relationship between wear and silver released in CrN-Ag coated lateralised bearings

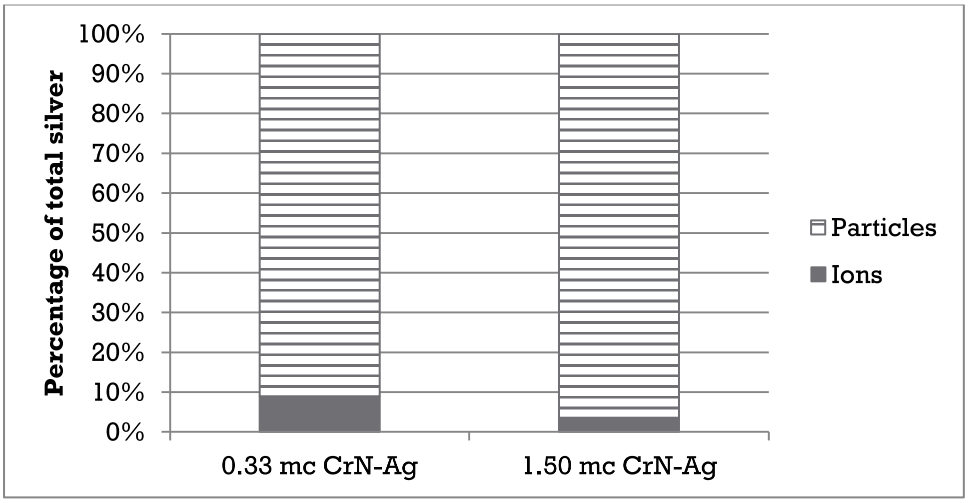


Figure 5:41: Proportion of ionic and particulate silver from CrN-Ag coating under lateralisation showing predominantly particles generated

The particles produced by these coated bearings appeared similar to those reported in the standard conditions CrN-Ag coatings, Figure 5:42. The distribution of these particles was similar to that observed under standard conditions with a mode of 12 nm, Figure 5:43. However, these did appear smaller (83% of particles <20 nm) than those reported under standard conditions (70% <20 nm).

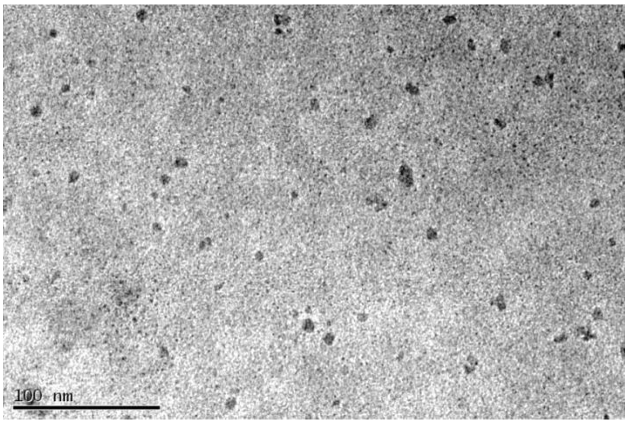


Figure 5:42: Particles produced by silver chromium nitride coated bearings under lateralisation conditions

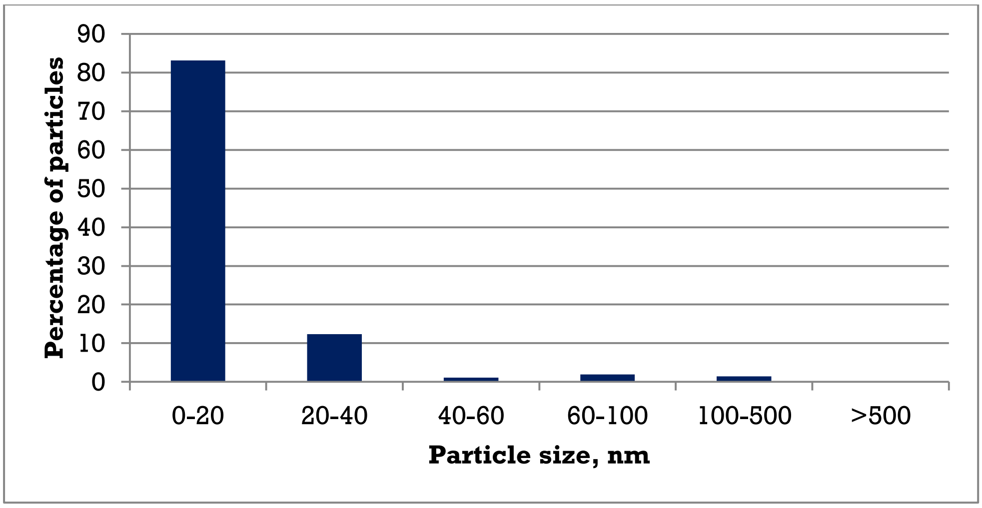


Figure 5:43: Particle distribution from CrN-Ag coatings under lateralisation conditions showing nanometre sized particles generated

5.4 Discussion

5.4.1 The influence of swing phase load

Metal-on-metal bearings have been well documented to produce low steady state wear rates under standard hip simulator conditions at values below 1.5 mm^3/mc (Fisher et al., 2006). Under these conditions, wear in the current study was also found to be low with a steady state wear rate of 0.40 ± 0.49 mm^3/mc. Although this mean wear rate was slightly higher than similar studies (0.26 ± 0.09 mm^3/mc) with the same sized 48 mm diameter bearings and the same double heat-treated cast metallurgy (Royle, 2012), this could be due to the small number of bearings tested in both studies. In the current study, 2 out of 4 of the bearings tested produced relatively high wear rates after 1 million cycles yet this was within the range reported in the literature, comparable to the 0.37 mm^3/mc reported in 50 mm diameter metal-on-metal bearings (Li et al., 2011), Figure 5:44.

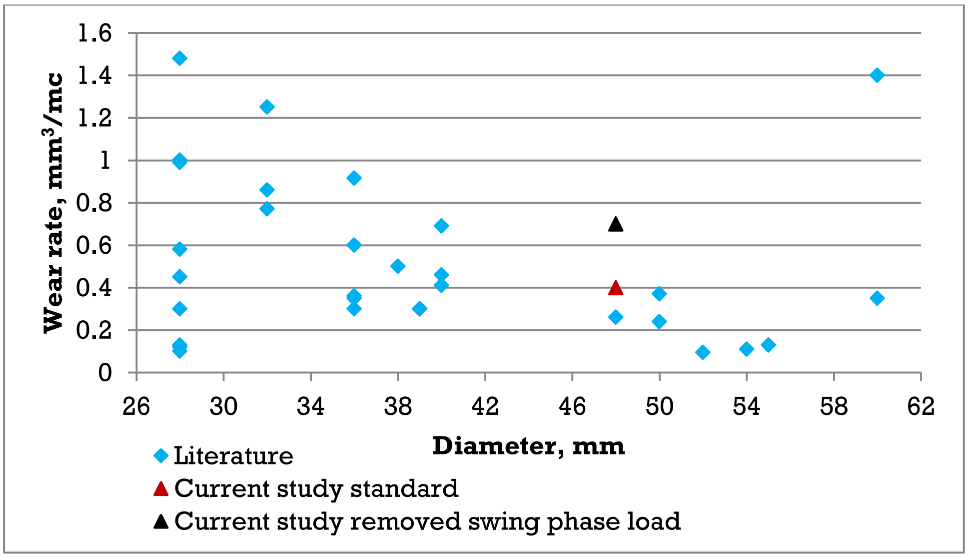


Figure 5:44: Steady state wear rates of metal-on-metal bearings under standard and removed swing phase load conditions in the current study compared to the literature

Although metal-on-metal bearings have been proposed as a low wearing alternative to metal-on-polyethylene bearings, retrieval wear rates as high as 87.73 mm^3/year have been reported using a co-ordinate measuring machine (Lord et al., 2011) compared to the wear rate of 0.40 ± 0.49 mm^3/mc recorded in the laboratory as in this work. There also appears to be an inherent variation in the clinical wear of metal-on-metal bearings with wear measured using roundness machines ranging from 1.63 to 7.48 μm/year in bearings without pseudotumours (Kwon et al., 2010), equating to approximately 0.08 to 0.38 mm^3/year (Medley et al., 1996). The variability has been reported to be greater in failed bearings (Kwon et al., 2010, Matthies et al., 2011b). Based on average wear rates, retrievals due to adverse reactions to metal debris show higher wear rates than revisions for other reasons (Lord et al., 2011) although the adverse reactions may be due to the increased wear of these bearings, Table 5:5.

Table 5:5: Mean wear rates reported in retrieved metal-on-metal bearings

Reason for revision	Number	Mean wear rate (range), mm^3/year	Study
Adverse Reaction to Metal Debris (ARMD)	18	17.64 (3.11-87.73)	Lord et al (2011)
ARMD fracture	2	68.50 (41.49-95.5)	Lord et al (2011)
Femoral neck fracture	4	5.95 (1.2-8.9)	Witzleb et al (2009)
Femoral subsidence	2	0.75 (0.4-1.1)	Witzleb et al (2009)
Avascular necrosis	1	0.51	Lord et al (2011)
Infection	1	3.98	Lord et al (2011)
Infection	1	0.7	Witzleb et al (2009)
Acetabular loosening	1	3.8	Witzleb et al (2009)

The variable wear behaviour of metal-on-metal bearings has also been observed in highly reproducible simulator studies under standard conditions with some bearings reaching steady state wear and others showing runaway wear behaviour (Bowsher et al., 2009). In many instances, these higher wearing bearings typically show a higher initial run-in period than other bearings (Bowsher et al., 2009, Vassiliou et al., 2006, Annissian et al., 2001). Various design changes influence this run-in wear rate such as clearance and diameter (Dowson et al., 2004a). Several explanations have been proposed for the runaway wear phenomenon including differences in contact pressure (Lee et al., 2010) or differences in the functional arc between bearings (Griffin et al., 2010).

However, these explanations fail to account for differences in wear between bearings of the same design and metallurgy under identical conditions.

Six wear trends of metal-on-metal bearings have been described by Bowsher et al. (2009), Figure 5:45; that of a classical high run-in and low steady state, three forms of "breakaway" wear in which a high run-in is combined with a period of high steady state wear which recovers to a lower wear rate and two "runaway" wear trends where wear remains high. In the current study, only (a), (d) and (f) wear patterns were identified for the components, although the increased wear rate of MoM S3 between 1 and 2 mc may have resulted in (b) or (c) wear patterns had testing continued.

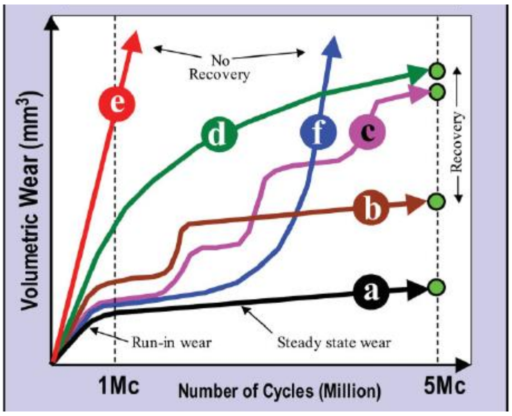


Figure 5:45: Graph showing the different wear trends documented in MoM bearings; a) classical run in and steady state behaviour, b-d) breakaway wear with recovery and e-f) runaway wear with no recovery. Image taken from Bowsher et al., (2009)

Higher *in vitro* wear in metal-on-metal bearings has been reported with the increasing proportion of wear in the cup (Bowsher et al., 2009). However, the current study observed wear to normally predominantly originate from the cup with this contributing to 80% of the total wear reported. Increasing proportions of head wear resulted in increased total wear suggesting that “well behaving” bearings can produce a significant proportion of wear from the cup. In the current study, three out of four bearings produced similar levels of cup wear throughout testing suggesting that the variation in wear reported between the three bearings were due to the heads. The remaining bearing (MoM S4) produced higher levels of both head and cup wear leading to greater wear overall. It is still unknown, however, what produced this increased wear. Bowsher et al., (2009) observed that under standard conditions, the smoother bearings with greater conformity exhibited higher wear rates, contrary to predictions derived from tribological theory. Therefore, it may be small changes within the design or material which produce significant effects on wear such as the presence and location of carbides.

The reduction of swing phase load from 280 N to 100 N has previously been shown to decrease steady state wear of metal-on-metal bearings fourfold (Williams et al., 2004b). A more pronounced run-in wear reduction was observed from 2.03 mm^3/mc to 0.13 mm^3/mc (Williams et al., 2006), although this study considered run-in wear up to 1 million cycles. The removal of swing phase load, in the current study, showed a 2.5 times reduction in run-in wear rate (0-0.33 mc) and 1.3 times reduction in transition wear rate but a 1.7 fold increase during steady state wear. This increased steady state wear in the current study could be due to the separation of the head and cup during the swing phase which may have produced uncontrolled and intermittent rim loading as a result of the hip wear testing machine design. This was particularly observed between 2-5 mc with increasing head and rim damage, preventing wear from reaching the steady state rate reported under standard conditions. The steady state wear rates observed with the removal of swing phase load may represent a more clinically relevant condition as rim contact and microseparation probably does not occur with every step. Although this difference in steady state wear was not as noticeable over 2 million cycles, over extended testing periods this increased wear rate would produce significantly more wear in the removed swing phase load condition bearings. Extrapolating the wear rates reported in the current study, after 4 million cycles the standard condition bearings would produce lower wear (2.55 mm^3) compared to the removed swing phase load bearings (3.07 mm^3), or a difference of 2.57 mm^3 at 10 million cycles emphasising the increasing difference between wear conditions and the need for appropriate test duration and conditions.

Cobalt released throughout testing showed a strong linear relationship with wear; levels produced under standard test conditions were similar to those previously reported (Royle, 2012). Despite the linear relationship between wear and cobalt release under both test conditions, these correlations were slightly different between conditions. Under standard conditions the linear relationship observed suggested greater levels of cobalt were released than when the swing phase load was removed if wear was equivalent. It is possible that the loading altered the cobalt release producing greater ionic loss under standard conditions. It has been recognised that increased loading can increase corrosion of the CoCrMo alloy (Yan et al., 2009), possibly suggesting mechanical induced corrosion. Changing the loading of the hip simulator, therefore, may have altered the amount of corrosion, resulting in greater corrosion during the standard loading. The removal of the swing phase load and subsequent separation of components may have also allowed the bearing surfaces to reform a passivation layer on the bearing surfaces thereby preventing additional cobalt release.

Despite possible changes in corrosion, the particles produced under both loading conditions showed little change in the size or shape of particles generated although a greater proportion of particles sized larger than 100 nm were observed under standard conditions. This, too, may have influenced the increased cobalt release as larger (80 nm) particles have been reported to corrode faster than smaller (20 nm) particles (Raghunathan et al., 2013) presumably due to a greater surface area. The particles produced during both test durations were predominantly round as reported in other studies (Billi et al., 2011b, Lu et al., 2012, Brown et al., 2006). The particles produced in the current study were smaller than reported previously with the mode particles sized 13 nm compared to 27 ± 13 nm reported by Lu et al., (2012). The size of the particles in the current study (< 500 nm) did, however, fall into the range of 8 to 116 nm reported (Brown et al., 2006).

5.4.2 Lateralisation damage in metal-on-metal bearings

Metal-on-metal wear has been shown to increase under lateralisation conditions in other simulator studies (Williams et al., 2004a). The steady state wear rate in the current study increased to 0.68 ± 0.33 mm^3/mc, a 1.7 fold increase from standard wear conditions. However, these bearings possessed similar steady state wear rates to the swing phase removed bearings which suggests that the wear rate produced by edge loading may not be dependent on the frequency at which it occurs i.e. with every step or not. The lateralisation wear rates reported here are, however, lower than other studies, Figure 5:46, although the relative increase in wear rates compared to standard wear conditions are similar (Williams et al., 2004a, Williams et al., 2007). Specifics in the design of the test components in the current study in comparison to those tested elsewhere may have influenced the low lateralisation wear achieved. In previous studies, small clearances of 50 μm have been utilised but the bearings presented in the current study have larger (150 μm) clearances. The use of this larger diameter and higher clearance in the current study should, according to lubrication theory, provide more favourable lubrication (approximate λ ratio of 2.7) over the 28 mm diameter bearings with a 50 μm clearance (approximate λ ratio of 1.3) (Dowson, 2006). A larger clearance, while not considered ideal under standard conditions, requires a larger separation to produce rim contact (Mak et al., 2002). Therefore, an increased clearance, as in the current study, may allow for more resilience to a specific distance of lateralisation than a smaller clearance. Small clearances have been recognised as a risk factor for edge loading clinically (Underwood et al., 2012).

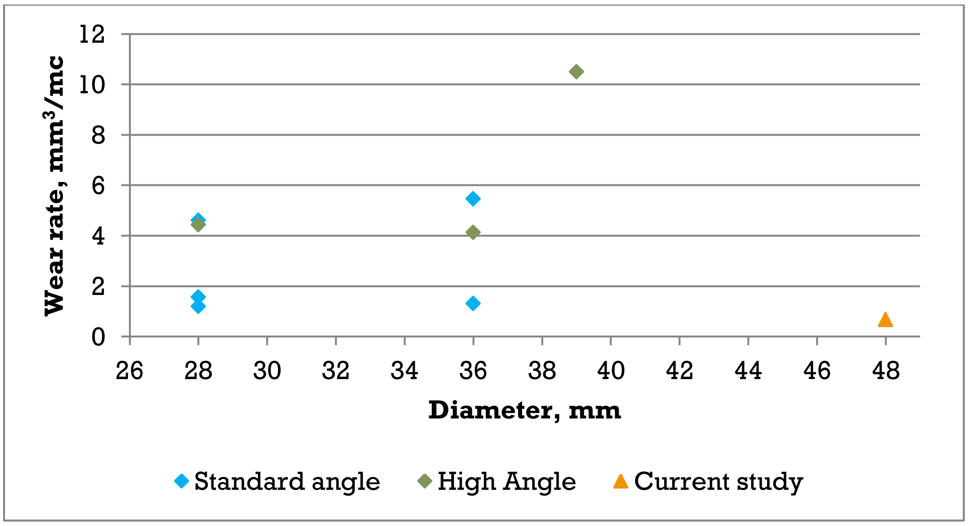


Figure 5:46: Steady state lateralisation wear rate in metal-on-metal bearings of the current study compared to results presented in the literature

The use of larger diameter may also have influenced the response to edge loading. Previous studies have not considered lateralisation wear of bearings above 40 mm diameter although, no difference was found when increasing diameter from 28 to 36 mm (Al-Hajjar et al., 2013b). Increasing the diameter has been reported to increase the coverage arc in some designs (De Haan et al., 2008) with the bearings used in the current study and those used by Al-Hajjar et al., (2013b) recognised to possess this increasing coverage arc with diameter (Underwood et al., 2012). In the current study, the bearings possessed a coverage arc of 155° while the ASR coverage arc can be as small as 144° (Bernthal et al., 2012). The coverage arc of the cup could, therefore, also affect the resistance to lateralisation conditions. The coverage arc in metal-on-metal bearings can increase the 45° inclination of a cup to an effective cup inclination between 50 and 63° dependent on design (Jeffers, 2012) and is attributed to the increased wear rates observed in some bearings at high inclination angles. Increased wear rates have been reported in some bearings with reduced coverage arcs when combining lateralisation and high angle conditions (Leslie et al., 2009b) suggesting an increased severity in bearings susceptible to high angle conditions. In bearings resistant to high angle conditions, no difference in lateralisation wear rates have been reported at angles of 45 and 65° although wear stripes were deeper in the high angle case (Al-Hajjar et al., 2013b). Therefore, lateralisation wear rates may be influenced by the coverage arc with bearings with smaller coverage arcs, and therefore at greater risk of edge loading with the cup's rim closer to the wear area of the cup, more sensitive to lateralisation conditions as smaller movements are required to initiate contact.

The majority of clinical reports of metal-on-metal wear have reported less than half of the wear to occur in the head, Figure 5:47. In contrast, standard hip simulator studies have reported the majority of wear to occur in the head (Royle, 2012, Williams et al., 2006, Barnes et al., 2008) with increasing proportion of wear occurring in the cup with the introduction of adverse conditions (Royle, 2012, Williams et al., 2006). The introduction of lateralisation in the current study led to increases in the proportion of head wear up to 1 million cycles, due to the presence of the additional wear stripe on the head. After 2 million cycles, the proportion of head wear showed little increase, maintained at around 45%. This greater proportion of head wear was combined with increased wear compared to standard testing. The scratches in the wear stripes produced were of similar depths to that reported in other metal-on-metal lateralisation studies (Al-Hajjar et al., 2013b, Williams et al., 2004a, Leslie et al., 2009b).

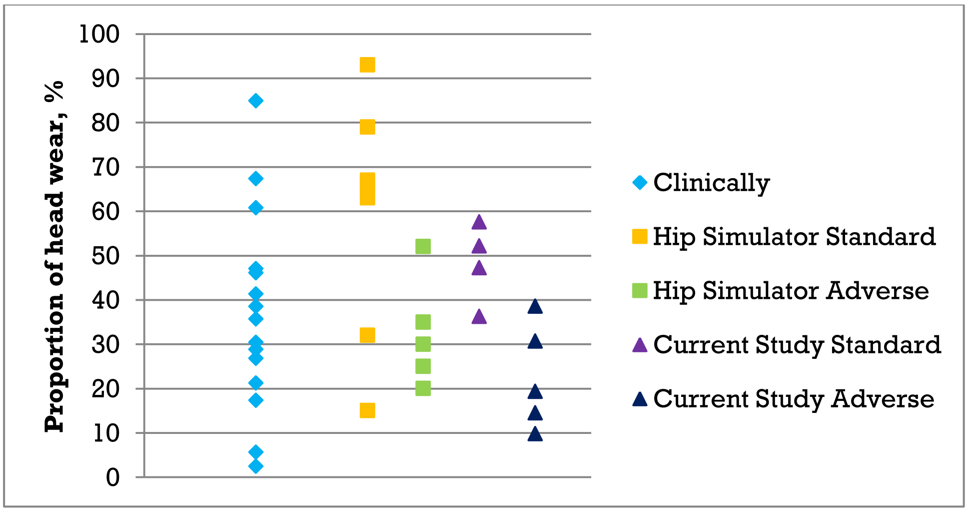


Figure 5:47: Reported percentage of head wear in metal-on-metal hip bearings from clinical and hip simulator studies

As a result of the relationship between wear and cobalt release, the cobalt released also increased with lateralisation conditions. However, the linear relationship reported under these conditions suggested that cobalt was released even when wear was not measured highlighting the limitations of gravimetric wear methods suggesting the wear reported may be underestimated. Proteins in the test fluid are known to adhere to the metal (Wimmer et al., 2003) which may result in mass gain of the bearings. Although cleaning attempts to reduce this, mass gain was reported at times in the current study. The loss of cobalt from the bearings is of greater concern than the volume loss of the components, as the wear products generated are probably the cause of the adverse biological responses seen clinically (Hart et al., 2012).

The cobalt produced was mainly ionic in form rather than particulate, more so than in the standard test conditions. This could be due to the longer storage time of the lateralised test fluid compared to the standard test fluid allowing for decomposition of the particles as observed in section 3.1. The lateralised bearings may have saturated by the time of measurement to 88% ions while the standard bearings were still decomposing. The standard condition bearings were stored for 2 months and 2 weeks before measurement in the 0.33 and 1.5 mc samples respectively which may explain why approximately 70% of the 0.33 mc sample was ionic compared to the 65% of the 1.5 mc sample.

The particles produced under the lateralisation conditions were overall, larger than those generated under standard conditions but still nanometre sized. In 39 mm diameter lateralised bearings larger particles of mode 30-39 nm have been reported (Leslie et al., 2009b) while smaller diameter bearings have not reported a significant change in particle size ranging from 8 to 107 nm (Brown et al., 2006). Larger metal particles may increase the micronuclei aberration in comparison to the smaller nanoparticles (Raghunathan et al., 2013) with other studies suggesting that larger, micron sized metal particles may generate immunological sensitivity over time (Brown et al., 2013). However, some studies have reported that the size of the nanometre particles is not as important as particle volume (VanOs et al., 2014) suggesting that the increased wear rate observed during lateralisation conditions may be more significant than a change in particle size distribution.

5.4.3 The use of CrN-Ag coatings

The use of coatings in metal-on-metal bearing has been considered with ceramic coatings on one or both bearing surfaces. The use of a silver doped chromium nitride has previously been proposed to both reduce wear and cobalt release and also to provide potential benefits from the antimicrobial silver wear products (Royle, 2012). The amount of silver added is crucial to maintain low wear rates whilst providing significant amounts of silver to produce antimicrobial properties. Testing of these coatings has shown low wear with high silver content (Royle, 2012), attributed to the self-lubricating property of the silver in the coating (Mulligan et al., 2010). The generation of homogenised 51wt% Ag-CrN coatings has shown to be resistant to wear and release large amounts (1,023 ± 67 ppb) of silver during 2 million cycles of simulator testing (Royle, 2012). This coating has been further adapted in the current work to produce increased or decreased silver content at the bearing surface.

In the current study it has been shown that wear and silver released increased with increasing silver surface concentration. Silver chromium nitride is softer than chromium nitride suggesting that the hardness of the surface and therefore the surface silver content is more influential on the wear rate than the coating's bulk properties. The initial wear of the silver rich coating, however, was exceptionally high and scouring damage was observed in the bearings suggesting that "normal" wear behaviour had not occurred. This damage has been attributed to the presence of a hard contaminant which may represent an adverse condition in which a third body particle may have been present, however as the contaminant could not be identified, the clinical relevance of this contaminant cannot be determined. Within 0.17 mc of testing in the presence of this hard contaminant, wear and silver concentration was as high as 4.75 mm^3 and 5,980 ppb respectively. Features of the wear patches of the cups within these damaged bearings was measured; it was observed in sectioned areas of the cup that wear occurred to a depth of approximately 5.5 μm, Figure 5:48. The total available silver can be calculated from this volume suggesting that for a circular wear patch of 10 mm diameter, 1538 ppb of silver would be available to be released. The cups contributed to at least 47% of the total wear therefore a maximum of 3272 ppb of silver could have been released. The least damaged silver rich CrN bearing (CrN-Ag+4) producing 65% of wear from the cup was estimated to produce 2,366 ppb of silver, similar to the 2,165 ppb measured suggesting that the damage in this bearing did not significantly influence the silver release. The three other bearings produced greater silver levels possibly due to the additional scouring damage generated by the contaminants and not representative of that generated by a "standard" wear process. This damage only resulted in a small area of the substrate to be exposed which is promising given the delamination of other coatings has previously been observed (Leslie et al., 2013). Indeed, low levels of cobalt were released from the bearings in the current study, even with this damage which suggests that the Cr adhesion layer remained intact and was harder than the contaminant.

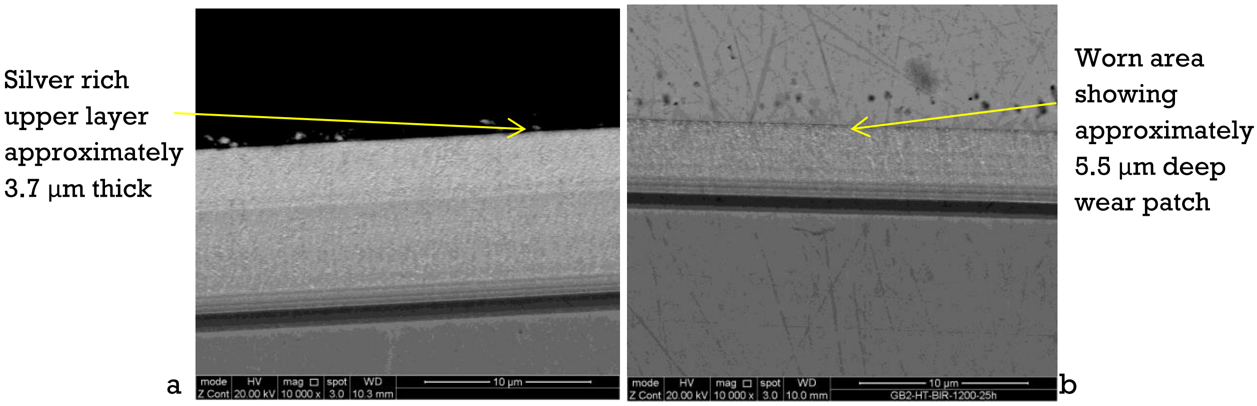


Figure 5:48: Scanning electron microscope images of sectioned cup in (a) unworn area and (b) wear patch courtesy of Adrian Leyland, University of Sheffield showing removal of the silver rich upper layer during the wear process

The rotation of the cups to an unworn and undamaged area produced significantly lower wear rates in the silver rich surface CrN coatings but this was still significantly higher than uncoated metal-on-metal and previous coatings, Figure 5:49. This high wear was probably increased due to the damage on the heads but the coating still prevented cobalt release whilst producing 3,720 ± 360 ppb of silver over 0.17 mc, equating to a molar concentration of 34.5 µM (34500 nM). Over 99% of the silver produced was particulate possibly as bovine serum has been reported to bind to silver nanoparticles, preventing dissolution (Ostermeyer et al., 2013). The generation of particles as opposed to ions may be beneficial as lower concentrations of silver particles have been reported to induce antibacterial effects compared to ionic silver, Table 5:6 and the toxicity of silver has been attributed to silver ions rather than particles (Ostermeyer et al., 2013). Biological tests have shown the minimum inhibitory concentration of silver to be 13.2 nM against yeast, 6.6 nM against Escherichia coli (E.coli) and greater than 33 nM against Staphylococcus aureus (St.aureus) (Kim et al., 2007). This suggests that the silver released from these bearings over approximately 2 months *in vivo* may indeed induce an antimicrobial effect. Others have reported higher concentrations of particles required, although still 100 times lower than the ionic concentration required, dependent on the particle shape (Pal et al., 2007). Spherical particles, as those produced in the current study, are required at higher concentrations (approximately 12 times greater) than truncated triangular particles. As the levels of silver produced are significantly higher than the minimum inhibitory concentration, there may also be concern over toxicity. Silver toxicity has been reported leading to discolouration of the skin and eyes as well as irritation of the liver and kidneys. The World Health Organisation has stated the No Observable Adverse Effect Level (NOAEL) of silver over a lifetime is 10 g (Lansdown, 2010). In the bearings in the current study, 2.23 mg of silver were produced over 0.17 mc, therefore at this rate over 700 million cycles would be required to produce a toxic effect.

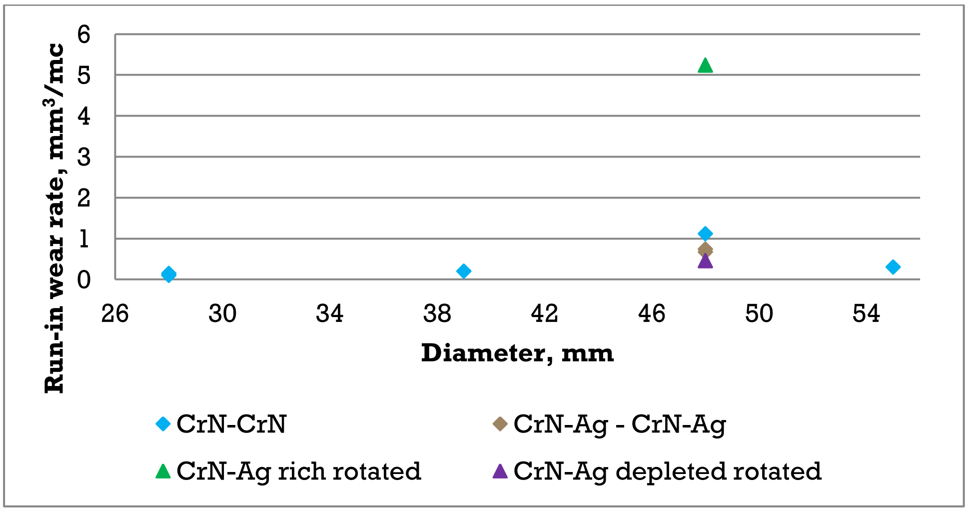


Figure 5:49: Run-in wear rates of CrN-Ag bearings in this study (triangles) compared to the literature (diamonds)

Table 5:6: Summary of the minimum concentrations reported to be effective against bacterium

Silver form	Bacterium	Concentration, nM	Study
Particulate	*E.coli*	3.3	Kim et al., (2007)
	St. aureus	33	
Particulate (spherical)	*E.coli*	116	Pal et al., (2007)
Particulate (triangular)		97	
Ions	*E.coli*	92, 705	Feng et al., (2000)
	St. aureus	92,705	

The silver depleted surface chromium nitride coatings produced lower wear rates than the silver rich surface chromium nitride coatings. This coating produced results comparable to chromium nitride and silver chromium nitride coatings (Royle, 2012, Williams et al., 2004a) and produced 140 ± 50 ppb (1.3 μM) of silver within the first 0.17 mc of testing and minimal cobalt suggesting that a small amount of silver was present at the surface. This small amount of silver released may still induce a biological response and as with the silver rich coatings, the silver was generated predominantly in particulate form with particles produced by the different coatings showing little difference in size. Despite the lower concentrations of silver measured in these bearings, these may still be greater than the minimum inhibitory concentration of silver required to produce an antibacterial effect.

The silver depleted surface chromium nitride coatings also showed a robustness to lateralisation conditions. Wear increased compared to standard test conditions but was maintained at 0.65 ± 0.07 mm^3/mc. This is higher than other CrN coatings under similar conditions, reported to be 0.55 mm^3/mc (Williams et al., 2004a). This difference may have occurred as the silver CrN coatings in the current study were not polished, while the CrN coatings in other studies have been and therefore additional wear in the form of microdroplet removal may have occurred. Wear in the current study has been determined based on the density of 51 wt% Ag-CrN, yet the surface of the coating may be closer to the density of pure CrN, thereby producing a higher estimation of wear rate to 1.07 mm^3/mc, Figure 5:50. This is still substantially lower than 18.04 mm^3/mc reported in failed CrN coated under lateralisation conditions (Leslie et al., 2013).

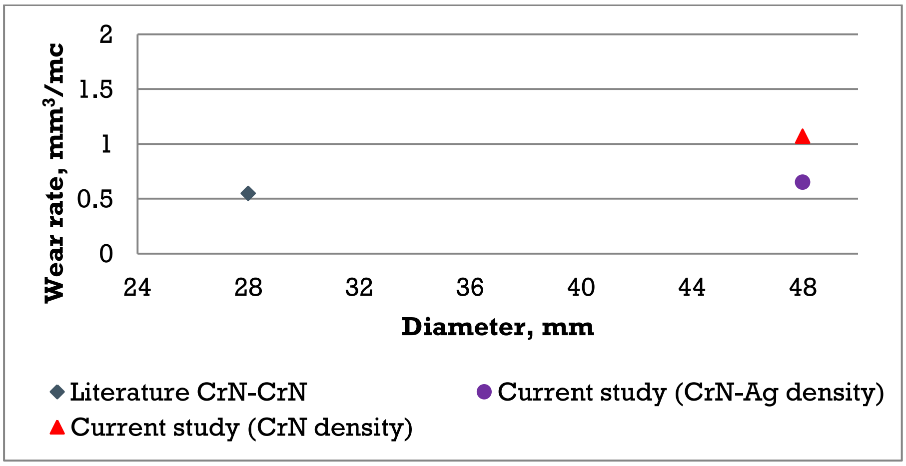


Figure 5:50: Wear rate of lateralised coatings which did not result in coating failure

The silver CrN coatings did not follow the same wear pattern as metal-on-metal, with a steady state wear rate throughout. Other CrN coatings have not shown this, with wear increasing after one million cycles in both "well behaving" and failed components (Leslie et al., 2013). Indeed, in these failed bearings the wear can reach approximately 50 mm^3/mc, two orders of magnitude higher than the steady state wear rate reported in the Ag-CrN bearings. The presence of an initial, higher run-in may be beneficial as the coating would release a higher dose of silver within the first week potentially reducing post-operative infections, preventing a biofilm to be established, although over the first 0.17 mc of testing 1,565 ± 571 ppb (15 μM) of silver was produced which should still induce a biological response. 15-30 μM (as produced in the current study) has been shown to make antibiotics more effective against E.coli as this makes the cell membrane more permeable (Morones-Ramirez et al., 2013). Although the surface of the coating possessed little silver, after 5 million cycles (approximately 5 years in an inactive patient) 18,786 ± 8,153 ppb (174 μM) silver was produced. Based on estimations to predict silver release used in the damaged high silver bearings, it would appear that the surface layer of the coating may be approximately 12wt% silver. As the initial low silver layer wore through, greater amounts of silver would be exposed which may explain the increasing rate of silver release observed as well as the increasing proportion of particulate silver. The exposure of this softer coating may have also increased wear leading to a constant wear rate throughout testing.

Although the majority of silver measured was in particulate form, the ionic silver measured may have been generated by diffusing through the coating during testing. This has been observed in magnetron sputtered silver CrN coatings capped with a CrN surface layer allowing for controlled, steady release of silver maintaining the beneficial lubrication properties. The thickness of this CrN cap, from 10 to 1000 nm, showed decreasing silver diffusion with increasing CrN thickness (Papi et al., 2012). In the lateralisation test, approximately 5 to 10% of the total silver concentration was ionic. In order to increase silver transport through the coating, increased temperatures as high as 550°C may be required

(Mulligan et al., 2010). Therefore, it seems that the amount of ionic silver available may be limited *in vivo* which would reduce the chances of toxicity.

The silver CrN coating of the current study produced wear stripes on the heads under lateralisation conditions similar to the metal-on-metal bearings and did not show any failure of the coating which was further confirmed with low cobalt levels reported in the lubricant throughout testing. Therefore, it seems that this silver chromium nitride coating may be able to withstand clinically relevant adverse conditions designed to challenge the adhesion of the coating and produce lower run-in wear rates than metal-on-metal bearings. Low steady state wear rates, comparable to metal-on-metal, and minimal cobalt release has also been observed, thereby potentially reducing the risk of hypersensitivity reactions while promoting an anti-microbial affect against infection.

5.5 Conclusions

Metal-on-metal wear is susceptible to edge loading although the extent to which this increases the wear rate may be design dependent in a similar manner to high angle conditions. The adoption of silver chromium nitride coatings can produce comparable or lower wear rates compared to metal-on-metal while also preventing cobalt release and additionally promoting the generation of particulate silver. The wear rate and the amount of silver released, however, are dependent on the silver surface concentration; both coatings in the current study produced silver at levels which may produce an antibacterial response. The low silver surface silver chromium nitride coatings have been shown to withstand clinically relevant adverse conditions, which has led to failure to other coatings, and release silver at a consistent rate over 5 million cycles.

6 Final Discussion

Hip replacement procedures have been in regular use for over 60 years and over this period have seen improvements in materials and designs. The hip replacement procedure is generally a success but all artificial hips have limitations compared to a healthy natural hip, which are often attributed to tribology. According to the England, Wales and Northern Ireland National Joint Registry (2013), 10,040 revision procedures were undertaken in the year 2012, an increase of 1,401 (20%) from the previous year. The Australian Joint Registry (2013) reports a 28.4% increase in revision procedures over a 9 year period from 2003 to 2012 whilst the Swedish Joint Registry (2012) reports an increase in revisions from 14.5 % of all hip procedures in the period 1991-1993 to 24.3% in a more recent 2 year period between 2009 and 2011. The increased number of revisions are, in part, due the increased number of primary replacements performed, with a small rise in the proportion of patients aged below 70 years old (Garellick, 2012, Graves, 2013) combined with increased patient lifespan. Recent issues surrounding metal-on-metal bearings (Willert et al., 2005) as well as the recall of DePuy's ASR prosthesis in 2010 (Cohen, 2011) have also contributed to the increased revision rates in THRs. After 12 years, the cumulative percentage revision of metal-on-metal bearings has been reported as 18.6% with the main causes of revision cited as pain and loosening (Graves, 2013, Powers-Freeling, 2013). Metal-on-crosslinked polyethylene, in contrast, has a cumulative revision rate of 5.4% after 12 years due primarily to loosening and dislocation (Graves, 2013, Powers-Freeling, 2013), although there are other contributing differences in patient population between these groups such as age, activity level and gender which can influence the revision rate.

The premature failure of the ASR and the high revision rates of metal-on-metal bearings were not predicted by extensive simulator tests although this was not the first incidence of unpredicted problems reported in hip replacements. In the 1960's when total hip replacement was being developed, Charnley reported disastrous levels of wear with the adoption of a PTFE cup (Dowson, 2001). In the late 1990s, the 3M Capital hip was recalled after reports of high revision rates (Hardoon et al., 2006) due to increased incidences of early femoral loosening attributed to a minor design change of the stem which resulted in a thin cement mantle (Massoud et al., 1997). In 2000, Sulzer Orthopaedics were forced to recall certain lots of their Intrer-Op acetabular shells after discovering that these had been contaminated by manufacturing oil (Eustice, 2001). These issues have all highlighted that need for appropriate post market surveillance as well as the need for new designs and modifications be fully evaluated through pre-clinical test methods. One aspect of this pre-clinical evaluation is the use of simulator studies with standardised methodologies developed to allow for comparison between laboratories (Affatato et al., 2008b). However, even following the current regulatory testing guidelines, the increased wear of the ASR in clinical use was not predicted. Many have attributed this clinical phenomenon to result from a sensitivity to increased cup inclination as a result of low cup coverage (Langton et al., 2008). This has challenged the relevancy of simulator testing as a method of pre-clinical screening with a growing consensus that more aggressive or challenging testing methods need to be adopted which are appropriate to the material and design of the components as well as clinical conditions.

The work in this thesis has considered the use of metal, polyethylene and ceramic coated bearing surfaces under different wear conditions representing different clinical wear modes. It has been acknowledged already that standard test conditions replicating McKellop's wear mode 1 tends to represent an idealised condition underestimating wear in all bearing combinations. Wear mode 2, representing edge loading increases wear and cobalt release in metal-on-metal bearings as reported in this thesis and elsewhere (Al-Hajjar et al., 2013b). In bulk ceramics, these lateralisation tests have produced clinically relevant wear rates (Al-Hajjar et al., 2013a) and have challenged the brittle nature of the material, in some cases leading to fracture (Stewart et al., 2003). In ceramic coated metal bearings, this condition has also increased wear rates and challenged the adhesion of the coating (Leslie et al., 2013) all suggesting that mode 2 wear conditions are a relevant adverse wear model in hard-on-hard bearings. Mode 3 wear, considering abrasive conditions, has predominantly been shown to increase the wear rates reported in metal-on-metal and metal-on-polyethylene bearings (Wang and Schmidig, 2003, Halim et al., 2014). Damage generated on the bearing surfaces before testing has increased the wear rate of metal-on-metal and metal-on-polyethylene (Hardaker et al., 2011, Barbour et al., 2000) suggesting that abrasive conditions represent adverse conditions in these combinations which is supported by the work within this thesis. No significant damage was observed in the ceramic coated bearing surfaces after abrasive testing in this thesis suggesting the ceramic coating developed as part of this work is resistant to this condition.

One of the benefits of adverse testing is the ability to investigate the influence of different parameters independently to create a better understanding of clinical wear and to build on the knowledge acquired through retrieval analysis, replicating failure modes at an accelerated rate. In polyethylene bearings particularly, where optimisation of the material has been progressively achieved and bearings can last decades, accelerating wear through damage and abrasion may allow for further focus on optimisation routes. Testing in conditions which are beyond clinically relevant may be required to distinguish between design modifications.

A primary concern with the use of metal bearing surfaces is the ionic products generated from the bearing surfaces and wear particles which may induce the hypersensitivity reactions observed (Cobb and Schmalzreid, 2006). Elevated blood ion levels have been reported in both metal-on-metal and metal-on-polyethylene bearings (Emmanuel et al., 2014, Almousa et al., 2013, Hartmann et al., 2012, Craig et al., 2014). In metal-on-polyethylene bearings, this phenomenon has been reported in larger (>36 mm diameter) bearings (Scully and Teeny, 2013). The latest England, Wales and Northern Ireland national joint registry report (2013) has also reported increased rates of revision in the larger (> 44 mm diameter) metal-on-polyethylene bearings although the cause of revision is not stated. It has been widely suggested that the problems associated with larger diameters may be due to the taper interface in which increased corrosion and fretting occurs (Cook et al., 2013, Dyrkacz et al., 2013). Taper corrosion has also been reported in the metal-on-metal bearings with some investigators reporting greater material removal from this interface than the bearing surface (Langton et al., 2011) although this has not been established in laboratory studies.

In simulator studies, ionic release into the test fluid has been monitored in metal-on-metal bearings (Fisher et al., 2004, Royle, 2012). The current work is the first to report cobalt levels in metal-on-polyethylene bearings and has shown a correlation between ion release and diameter. The small, 28 mm diameter bearings produced measurable levels cobalt even though they were significantly lower than the large diameter metal-on-polyethylene and metal-on-metal. There are issues attempting to correlate these *in vitro* concentrations to clinical concentration levels as the hip simulator studies performed in this thesis use approximately 600 mL of test fluid; however the total mass of cobalt produced can be determined, Table 6:1. A clinical concentration can be estimated based on the assumption that the hip joint contains 2.7 mL of synovial fluid (Moss et al., 1998) leading to a maximum concentration of 2,291 ppm of cobalt after 1 million cycles (1 year or less) under standard conditions in metal-on-metal bearings assuming 6.185 mg is released and without any cobalt migrating away. This is clearly much greater than that reported in the synovial fluid of patients (maximum of 14 ppm) which is explained by the cobalt migrating rapidly from the hip thereby lowering the clinical concentration observed. Studies considering cobalt levels in the urine of patients with metal-on-metal hip replacements have shown that some of these ionic products can be processed and removed by the body (Engh et al., 2009). The highest concentration of cobalt measured in urine produced over 24 hours is 14.22 ppb (Engh et al., 2009) which equates to a maximum of 28.44 μg assuming 2 litres of urine were produced over this time period (NIH, 2014). Over one year this would equate to a maximum of 10 mg that could be removed from the body, within the range of cobalt estimated in these laboratory tests. Lateralised metal-on-metal bearings and alumina third body tested metal-on-polyethylene bearings are the only conditions which produced a mass of cobalt after 1 million cycles greater than the amount predicted that would be removed. Adverse conditions may therefore represent more clinically relevant cobalt levels. Under clinically relevant adverse conditions, the cobalt concentration in the metal-on-polyethylene bearings was significantly lower than the metal-on-metal bearings possibly explaining why hypersensitivity reactions are less common in these bearings. However, this condition still elevated the cobalt levels and the largest amount of cobalt in all tests was measured in metal-on-polyethylene bearings tested with alumina third body particles. Third body abrasion has not been widely investigated in metal-on-metal bearings yet the damage generated in the metal surfaces of the current study due to alumina particles suggests that this abrasive condition may represent an extreme test conditions, further increasing cobalt levels in metal-on-metal bearings.

Table 6:1: Mass of cobalt produced in different bearings under different simulator conditions in this thesis and the subsequent calculated concentration experienced clinically. * assuming 2.7 mL in the synovial joint. ** Jogging only conducted to 0.0144 mc.

		Mass of cobalt, µg		Maximum synovial fluid clinical concentration, ppm*
Bearings	**Test conditions**	**0.33 mc**	**1 mc**	
28 mm MoP	Standard	15	30	11
	Bone Cement 3rd Body	37	89	33
	Damage	6	9	3
52 mm MoP	Standard	94	157	58
	Bone Cement 3rd Body	139	355	132
	Bone Cement Damage	40	113	42
	Alumina 3rd Body	6,956	42,414	15709
	Alumina Damage	120	503	186
	Jogging**	31		12
48 mm MoM	Standard	4,665	6,185	2291
	Removed Swing Phase	1,188	2,547	943
	Lateralisation	7,825	11,544	4276

Ceramics coatings have been proposed on the metal bearing surfaces to reduce cobalt release. Standard hip simulator conditions have shown both wear and cobalt reduction compared to uncoated metal-on-metal (Fisher et al., 2002). In the metal-on-polyethylene bearing, the results have been less promising under standard conditions due to the surface roughness achieved after coating (Galvin et al., 2008). The current work has considered three coatings; one CrN coating and two 51wt% Ag-CrN coatings with different levels of silver at the surface. Throughout all test conditions, no coating showed delamination although the silver rich surface Ag-CrN did show significant damage attributed to a hard contaminant and small numbers of bearings were tested. All coatings were successful at reducing cobalt levels compared to the uncoated components.

Clinically, delamination as soon as 1 year post implantation has been reported in titanium nitride coated metal-on-conventional polyethylene bearings (Harman et al., 1997). These results have led to adverse *in vitro* testing to focus on the adhesion of the coating to the substrate; some delamination has previously been reported in hard-on-hard bearings under adverse conditions (Leslie et al., 2013, Royle, 2012). Royle (2012) tests at performed high angle and introduced luxation damage on chromium nitride and silver doped chromium nitride coated metal-on-metal bearings. These tests generated failure in 17 wt% silver chromium nitride coatings, increasing the wear rate of these bearings and releasing cobalt. Leslie et al., (2013) and Williams et al., (2004a) focussed on the lateralisation conditions and induced delamination of chromium nitride coated metal-on-metal bearings. In this thesis, similar conditions in the low silver surface CrN-Ag bearings did not result in delamination and the wear rates of these bearings has been comparable or lower (0.65 ± 0.07 mm^3/mc) than those of uncoated metal-on-metal under the same conditions.

The chromium nitride coating in the current study tested against polyethylene under aggressive third body conditions designed to promote scratching and damage of both bearing surfaces, remained resistant to this abrasion, preventing delamination and maintaining a low surface roughness. The surface roughness of the CrN coated heads of the current study after polishing was low (Ra of 0.01 ± 0.01 μm), within surface finish requirements for ceramic bearing surfaces as described by ISO 7206-2 (2011). The post deposition polishing did not damage the coating.

Ceramic surfaces which are harder than the metal and polyethylene, have not shown embedding of third body particles while also providing additional abrasive resistance (Davidson et al., 1994, Wang and Schmidig, 2003). The inclusion of silver, however, reduces the microhardness of the coating from 13-14 GPa in the CrN coating to 6-7 GPa in the 51wt% Ag-CrN. The potential benefit of the silver added to these coatings, however, may be that it improves lubrication (Mulligan et al., 2010) and additionally provide an antimicrobial effect (Monteiro et al., 2009). Silver has previously been added to wound dressings although it is unclear whether these offer an improvement compared to conventional wound dressings (Aziz et al., 2012) as different dressings release different amounts of silver. Nanocrystalline silver dressings have been acknowledged to release the greatest quantity of silver (Leaper, 2006) over a prolonged period with reports that this wound dressing is more effective than other silver wound dressings (Fong and Wood, 2006). Within orthopaedics, silver nanoparticles have been added to bone cement yet have not been shown to be efficient at preventing infections in rabbits (Moojen et al., 2009) despite *in vitro* microplate proliferation tests showing resistance to S. epidermidis, methicillin-resistant S. epidermidis (MRSE) and methicillin-resistant S.aureus (MRSA) (Alt et al., 2004). Silver added to an area of titanium at a density of 20 mg/cm^2 has shown to be bactericidal while not effecting osteointegration (Coathup et al., 2012) allowing for use on hip replacement stems, yet silver in a bearing surface has never been clinically trialled. The incorporation of silver may be beneficial as 0.83 revisions per 1000 patients occur due to infection (Powers-Freeling, 2013). Although this can occur at any point after surgery (Anagnostakos et al., 2009) and therefore a continuous release of silver may help to prevent it, the greatest risk of infection occurs in the first 6 weeks following surgery (Valle, 2010). A sacrificial high silver layer, as in the silver rich surface coatings of this thesis, may therefore, provide an initial high concentration of silver reducing the risk of early infection. In the silver rich surface coatings, 2.23 mg of silver was produced within 0.17 million cycles equating to 825 ppm in a 2.7 mL hip joint, which could potentially induce an antibacterial effect as the reported minimum inhibitory concentrations required against E.coli and S.aureus equate to 0.4 and 4 ppb respectively (Kim et al., 2007). A lower silver containing bulk coating similar to that observed in the lateralisation testing could then produce low wear and withstand clinically adverse conditions, Figure 6:1. This would allow for continuous silver release as the low silver surface CrN bearings would produce 86 μg (32 ppm) in a 2.7 mL hip joint within 170,000 steps. Although 0.17 wt% Ag-CrN coatings have shown failure in hip simulator tests (Royle, 2012), the low surface silver levels of the coating tested in the current study showed minimal wear and no failure.

Figure 6:1: Schematic showing a proposed optimal silver CrN coating including a high silver surface to provide an initial increased silver wear rate

Clinical failure is often multifactorial in nature and therefore may require more multidisciplinary approaches to assess bearings. Indeed, it is the biological response to wear products that is often limiting in the success of the bearing and so in low wearing bearings, it may be more important to consider these products. The inclusion of vitamin-E in polyethylene appears to have a serendipitous effect in reducing inflammatory responses which may ultimately have larger impact in prolonging the lifetime of the implant than the oxidative stability it was designed for. Similarly, the inclusion of silver into a chromium nitride coating may reduce post-operative infections but requires *in vitro* testing, both mechanical and biological, to determine its likely success. Ultimately, it is difficult to fully predict all conditions and responses in the body and therefore, development of *in vitro* testing should be based on growing knowledge achieved through retrievals.

6.1 Future Work

Despite the promising results observed with the coatings considered in this thesis, further investigations performing additional adverse tests may be valuable in evaluating the chromium nitride and silver chromium nitride coatings. Lateralisation tests have produced the greatest damage in coatings (Leslie et al., 2013) yet this was not conducted in the CrN-on-polyethylene bearings as this was acknowledged to reduce polyethylene wear (Williams et al., 2003). Wear of the coated head was reported in the current study suggesting that the polyethylene may remove material from the chromium nitride bearing surface. It therefore, could potentially damage the head and possibly test the adhesion of the coating. Additional tests could also be devised in which the head could contact a harder, non-bearing surface such as the metal shell.

A silver chromium nitride head coating could also be paired with a polyethylene cup and subjected to similar test conditions as the chromium nitride coating of the current study. This coating has shown the potential to release anti-bacterial levels of silver in hard-on-hard pairings but the silver released would probably be reduced in a hard-on-soft combination and therefore, greater levels of silver may be required within the coating. These coatings would also need to be polished, as the chromium nitride coatings in the current study were, to remove microdroplets formed during the coating process.

The work within this thesis focussing on the use of silver chromium nitride coatings has led to the proposal of an optimised coating with a high "sacrificial" silver layer but this coating would also need to be developed and tested thoroughly, under standard and adverse, probably lateralisation, conditions. The scouring damage observed in the high silver surface chromium nitride coatings of this thesis suggests that coatings containing high levels of silver may be susceptible to abrasive test conditions and this, too, could be investigated.

The wear particles and ions produced in the silver chromium nitride tests suggest that the silver produced may behave an anti-bacterial agent but in order to confirm this, biological tests need to be performed on particles of the correct morphology. As the wear of these coatings is low, even under adverse tests, alternative methods to generate significant amounts of wear may need to be conducted and fully evaluated.

In metal-on-metal bearings, the exact causes of clinical failure in some bearings are not fully explained and therefore, it may be appropriate to develop more novel test simulator methodologies based on retrieval observations. One aspect to consider may be the replication of taper damage observed in metal-on-metal retrievals, a non-bearing surface and therefore a Mode 4 wear mechanism. Simulator wear tests determining taper damage have not been completed but it may be possible to focus on this and determine appropriate methods to accelerate wear at this interface. Isolation of the taper interface may also be of interest in metal-on-polyethylene bearings to determine the origin of the cobalt measured in this thesis. Coating of the taper could also be investigated although the geometry of the taper may present a challenge. Development of adverse testing of any proposed taper coating would also need to be performed to ensure robust adhesion as failure of coatings at the bearing surface has already shown to lead to excessive wear (Leslie et al., 2013).

The introduction of more corrosive conditions on the wear and ionic release of metal-on-metal bearings may also help the understanding of clinical failures. Yan et al., (2009) has reported the influence of metallic nanoparticles on the corrosion of metal-on-metal bearings, determining that these nanoparticles disrupt the passive layer on the surface leading to increased corrosion. Third body tests may be valuable test conditions for more than just wear in these bearings. It may be possible to develop the tests further to determine conditions which increase the corrosive potential on bearings under clinically relevant conditions and beyond. The storage of these wear particles may also be of interest as this thesis has shown degradation of cobalt over time even when stored at -20°C.

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Appendices

Appendix A: Cleaning Protocol*

1. Rinse with ultrapure water.
2. Using an electric toothbrush clean the bearing surface using a solution of ultrapure water and Decon 90 detergent for 5 minutes.
3. Rinse with ultrapure water.
4. Vibrate in ultrasonic tank in ultrapure water for 10 minutes.
5. Rinse with ultrapure water.
6. Vibrate in ultrasonic tank in a solution of ultrapure water and detergent for 10 minutes.
7. Rinse with ultrapure water.
8. Vibrate in ultrasonic tank in ultrapure water for 10 minutes.
9. Rinse with ultrapure water.
10. Vibrate in ultrasonic tank in ultrapure water for 3 minutes.
11. Rinse with ultrapure water.
12. Dry with a jet of clean nitrogen gas.
13. Soak in propan-2-ol for 5 minutes.
14. Dry with jet of clean nitrogen gas.
15. Leave to air dry for a minimum of 12 hours prior to weighing.

* For metal-on-metal components, double all times except for that stated in step 2.

Appendix B: Polyethylene particle isolation protocol

<u>STEP 1: DIGESTION</u>

1. In bottle with small magnetic stirrer, add 6 mL of 8 mol/L urea, 0.1mol/L HEPES buffer solution and 0.04% sodium azide with 3 mL of sonicated sample. Add 167 µg of Proteinase K (20 mg/mL). Leave on hot plate at 37°C, stirring for 18 hours.
2. Sonicate 4 times for 30 seconds each. In between each sonication, leave for 1 minute.
3. Add 167 µg of Proteinase K. Leave on hot plate for 24 hours.
4. Repeat sonication.
5. Add 167 µg of Proteinase K. Leave on hot plate for 5 hours.
6. Repeat sonication.
7. Add 750 µL 200mmol/L EDTA (60 mmol/L final concentration) and 850 µL of 0.5 mol/L TCEP, 0.1 mol/L HEPES, pH 7, 0.04% NaN_3 (final TCEP concentration 20 mmol/L). Leave for 3 hours.
8. Store for 18 hours.

<u>STEP 2; PURIFICATION</u>

PART 1:

1. Sonicate sample.
2. Using 14 mL centrifuge tube (medium size tubes), add 7 mL of sample

3. Add 2 mL 6 mol/L of Urea.
4. Add 3 ml of solution containing 20% sodium lauroyl sarcosine (SLS), 4 mol/L urea, 20 mmol/L EDTA, 50 mmol/L HEPES at pH 7.5 and 0.04% NaN_3
5. Centrifuge at 284,000g (SW41Ti 41k RPM) for 4 hours at 25° C.
6. Using pipette remove layer of particles (opaque layer near the top of tube).

PART 2:

1. Heat digested serum sample at 80° C for 20 minutes then sonicate x 4 for 1 minute
2. Add 2 ml of sample in a centrifuge tube (medium tube)
3. Add 1.5 ml 20% SLS in 2 mol/L Urea on top of sample
4. Add 2 ml 2% SLS
5. Layer 2 ml 20% isopropyl alcohol (IPA), 2ml 25% IPA, 1.5ml 30% IPA, 1 ml 100% IPA
6. Centrifuge the tube at 4446g for 30 minutes at 25°C (5k RPM SW41Ti rotor)
7. Centrifuge at 284,000g for 4 hours at 25°C (41k RPM SW41Ti rotor)
8. Using pipette remove opaque layer of particles (middle of tube)
9. Dilute sample with 100% IPA to a volume of 7 ml and leave overnight

PART 3:

1. Sonicate sample for 30 seconds x 4, separated by 1
2. Add 2 mL of 10% IPA into medium sized tube
3. Layer 3 mL of 40% IPA above this
4. Add 7 mL of sample on top of this
5. Centrifuge tube at 284,000g for 5 hours at 25° C (41k RPM SW41Ti)
6. Collect particles at interface between 40% and 10% IPA with pipette and store.

<u>DISPLAY</u>

1. Clean 5 x 5 mm silicon wafer by sonicating in propanol and coat with Cell-Tak glue.
2. Add 10 μL Cell-Tak to microfuge tube followed by 200 μg 0.2 mol/L HEPES (pH 9.2), 0.15 mol/L NaCl and 0.04% NaN_3. Mix by pipetting.
3. Uniformly spread 20 μL of solution over silicon wafer and incubate for 30 minutes at 25° C in a Petri dish
4. Remove excess glue by washing with 50 mmol/L HEPES (pH 7.5), 0.15 mol/L NaCl, 0.04% NaN_3
5. Use wafer immediately or store for up to 1 hour in 50 mmol/L HEPES (pH 7.5), 0.15 mol/L NaCl, 0.04% NaN_3
6. Sonicate purified sample and mix 125 μL of sample with 750 μL ultrapure water.
7. Add mixture to small centrifuge tube.
8. Place coated silicon wafer on clear plug (polycarbonate). Place in tube with wafer facing down.
9. Centrifuge at 84,000g for 4 hours (32k RPM small centrifuge MLS 50 rotor)
10. Remove wafer
11. Wash wafer with ultrapure water

12. Dry overnight

Protocol Validation

In order to determine the repeatability of this method, five samples were taken from the same bearing and time point and analysed using the above protocol. It can be seen in Figure A:0:1 that all distributions are bimodal but one showed distinctly larger particles to be more prevalent. This was attributed to the malfunction of the ultrasonic tank therefore it was determined that the protocol produced consistent results.

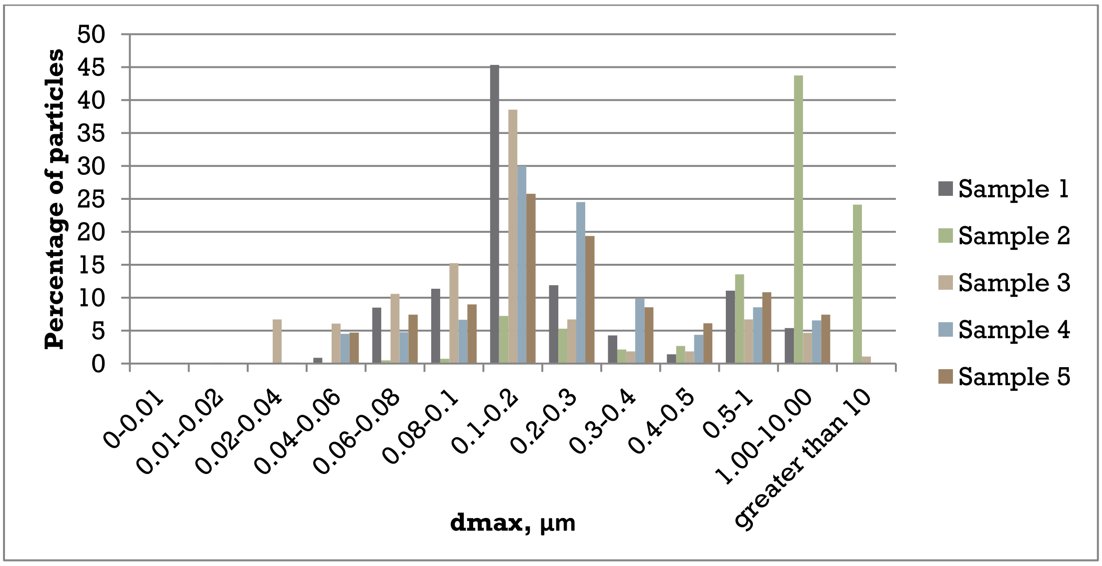

Figure A:0:1: Particle distribution from 3 samples of the same bearing

Three separate samples were taken from different stations at the same time point and showed similar distributions, Figure A:0:2, suggesting no difference between stations of the same bearing type at the same time point.

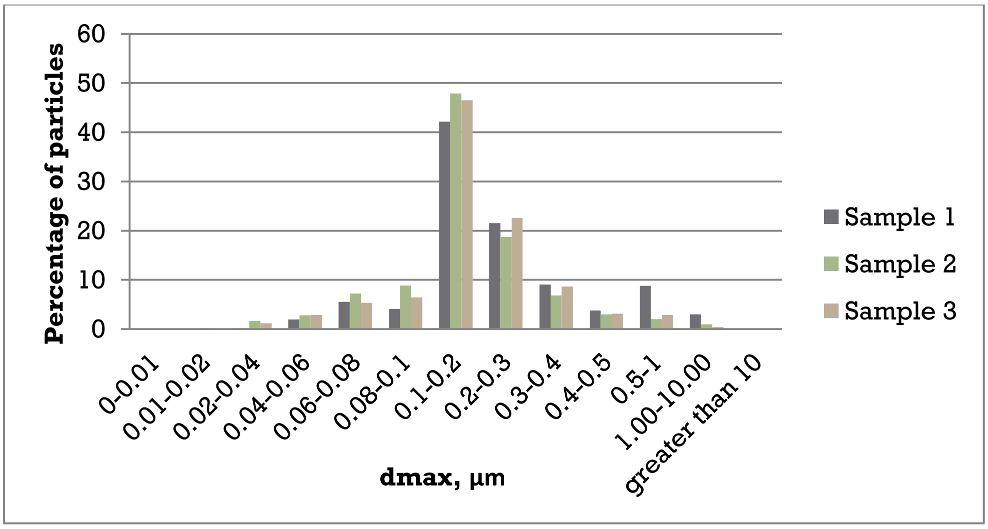

Figure A:0:2: Polyethylene particle distributions from three samples from three separate stations

Appendix C: Calculations to estimate volume loss due to impingement

The bottom of the 28 mm diameter liners showed impingement of the taper fixture leading to additional material loss and therefore an increased wear measurement, Figure A:0:3. This feature was elliptical in shape and Vernier calliper measurements of the length, *l*, and width, *w*, of this area were measured in each liner.

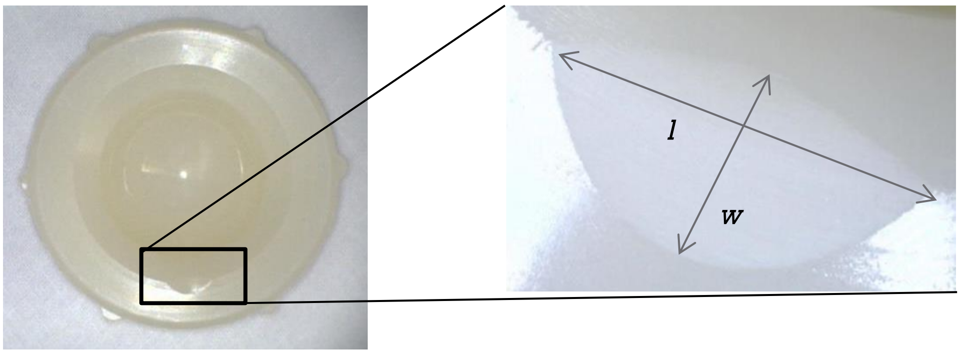

Figure A:0:3: 28 mm diameter liner after 0.33 mc of testing showing impingement and removal of material

The location of impingement between the taper fixture and the liner was known as were the dimensions of these components, Figure A:0:4. From this knowledge, the volume loss of the liner could be determined by calculating the volume, V, of two cones with elliptical bases, equation 5, in which the height, h, of the cone was determined through trigonometric functions. These two cones represented the material lost from the edge of the liner and the additional material lost due to the curve of the taper fixture.

$$V = \frac{\pi l w h}{3} \tag{5}$$

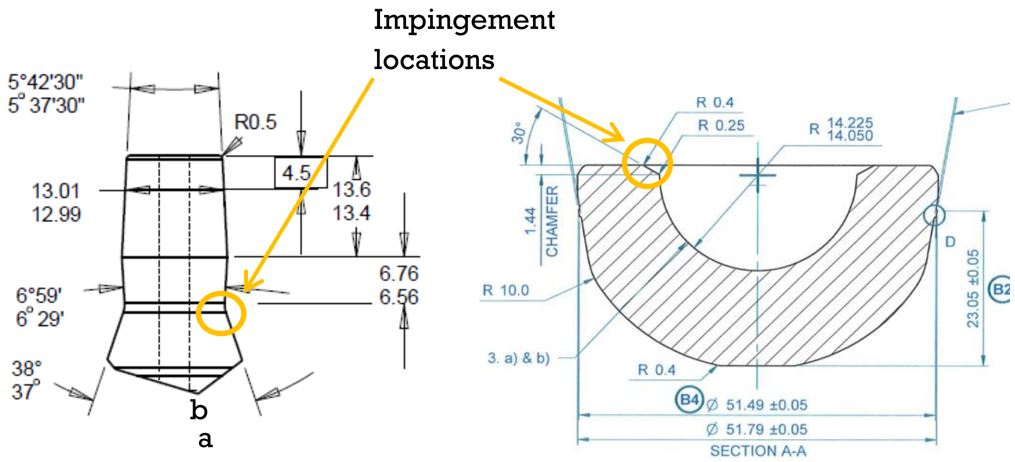

Figure A:0:4: CAD drawings showing the location of impingement in a) the taper fixturing and b) the 28 mm polyethylene liner

The impingement volume loss was similar between liners with approximately 2 to 3 mm^3 after 0.33 million cycles, Figure A:0:5. This impingement volume loss continued with testing but reduced from half of the gravimetric wear measured in the first 0.33 mc to a third of the wear after 1 million cycles.

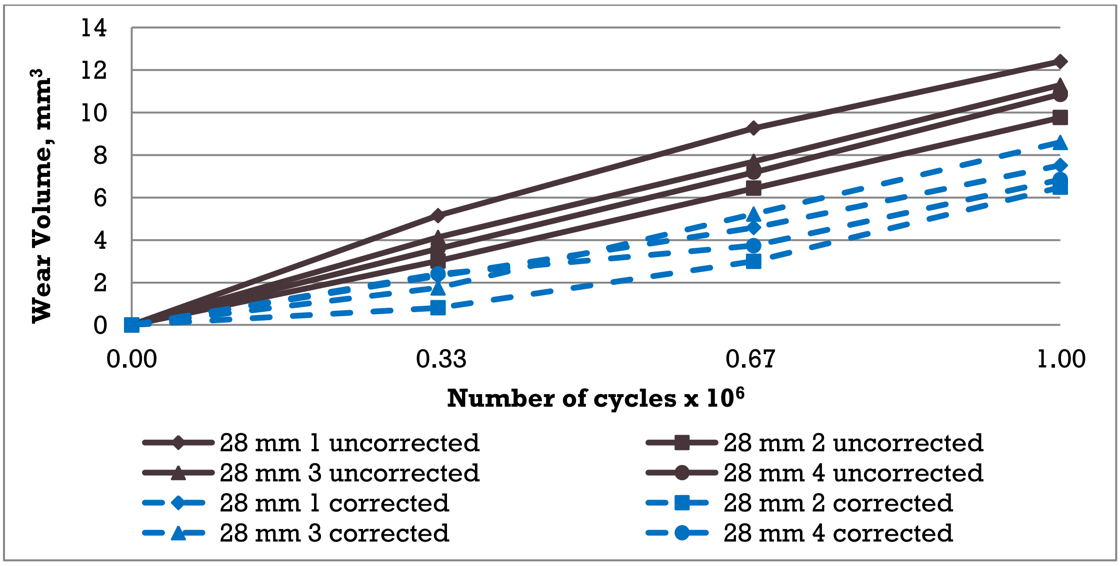

Figure A:0:5: Polyethylene liner wear volume for 28 mm diameter liners uncorrected and corrected for volume loss from impingement

Appendix D: Metal particle isolation protocol

STEP 1: DIGESTION

1. Centrifuge 5 ml of sample in centrifuge tube for 3 hours at 164,000g (40k RPM 70Ti rotor) and 25°C
2. Remove supernatant leaving 1 ml and pellet
3. Add 6 ml of 8mol/L Urea (0.1 mol/L) and HEPES (pH 7.5).
4. Add $CaCl_2$ (40mmol/L) and Proteinase K (0.5 µg/mL) to pellet
5. Mix in bottle with magnetic stirrer on hot plate at 37°C and for 24 hours adding 167 µL of Proteinase K at 0 and 18 hours with sonication (4 times at 1 minute intervals) before addition.
6. Add 750 µL 200mmol/L EDTA (60 mmol/L final concentration) and 850 µL 0.5 mol/L TCEP, 0.1 mol/L HEPES, pH 7, 0.04% NaN_3 (final TCEP concentration 20 mmol/L).

STEP 2: PURIFICATION AND DISPLAY

1. Dilute 10 µL CellTak glue and mix to 200 µL 0.2 mol/L HEPES (pH 9.2), 0.15 mol/L NaCl, 0.04% NaN_3
2. Spot 10 µL onto sheet of parafilm
3. Place TEM grid onto bubble of glue and incubate for 30 minutes
4. Wash in Petri dish with 50 mmol/L HEPES (pH 7.5), 0.15 mol/L NaCl and 0.04% NaN_3
5. Hold grid in a separate dish until needed (up to 1 hour)
6. Add 700 µL 2.0 g/mL cesium trifluoroacetate (CsTFA) to small tube followed by white (PTFE) plug
7. Transfer grid to top of plug and allow to sink to bottom.
8. Centrifuge at 25°C and 30,000g (20k RPM, bench top centrifuge MLS 50 rotor) for 15 minutes
9. Sonicate digested sample four times in 1 minute intervals
10. Layer 1200 µL 7 mol/L urea, 20 mmol/L EDTA, 50 mmol/L HEPES, 0.04% NaN_3 above CSTFA layer
11. Add 1200 µL digested sample.
12. Centrifuge at 37°C for 30 minutes at 3300 g (5k RPM MLS 50 rotor)
13. Centrifuge at 37°C for 4 hours at 84,000 g (32k RPM MLS 50 rotor)
14. Allow to dry.
15. Store in TEM box

Appendix E: Publications

List of publications:

Papers

1. Use of a chromium nitride coating against vitamin-E blended HXLPE hip bearings D.de Villiers, A. Traynor, S.N. Collins, S. Banfield, J. Housden, J.C. Shelton (2014) Clinical Orthopaedics and Related Research (under review)

Podium Presentations

1. Severe Wear Testing of Chromium Nitride Coated and Uncoated Metal on Highly Crosslinked Vitamin-E Blended Polyethylene Hip Bearings *Bath Biomechanics Symposium 2013 Bath, UK*
2. Wear of large diameter vitamin-E blended HXLPE hip bearings against uncoated and chromium nitride coated metal *6th International UHMWPE Meeting 2013 Torino, Italy*

Poster Presentations

1. Wear of vitamin E blended polyethylene against large diameter CoCrMo metal and EBPVD chromium nitride coated femoral heads
2. *European Orthopaedic Research Society 2012 Amsterdam, Netherlands*
3. Adverse testing in metal-on-metal and CrN-Ag coated hip replacements *Orthopaedic Research Society 2013 San Antonio, Texas*
4. Use of Chromium Nitride Coating for the Reduction of Cobalt Release and Metallic Wear in Metal-on-Polyethylene Bearings *Combined Orthopaedic Research Society 2013 Venice, Italy*
5. Adverse testing of uncoated and CrN coated metal heads paired with vitamin-E blended highly-crosslinked polyethylene liners *International Society of Technology in Arthroplasty 2013 Palm Beach, Florida*
6. The Use of a CrN Coating to Minimise Polyethylene Wear and Cobalt Release in Metal on Vitamin-E Blended Highly Crosslinked Hip Bearings *Orthopaedic Research Society 2014 New Orleans, Louisiana*
7. Wear Reduction in Polyethylene through the adoption of scratch resistant CrN coatings *European Federation of National Associations of Orthopaedic and Traumatology 2014 London, UK*
8. Determining appropriate adverse testing for coated metal-on-polyethylene hip bearings *World Congress of Biomaterials 2014 Boston, Massachusetts*

Paper Submitted to CORR

Use of a chromium nitride coating against vitamin-E blended HXLPE hip bearings

D.de Villiers, A. Traynor, S.N. Collins, S. Banfield, J. Housden, J.C. Shelton

Abstract

Polyethylene materials have been optimised to reduce wear and prevent long term oxidation of acetabular liners yet they are still susceptible to *in-vivo* roughening. In order to increase the scratch resistance of the counterface, ceramic heads have been adopted although their diameters are generally limited to less than 48 mm. The use of a chromium nitride (CrN) coating on a large metallic head is proposed as an alternative. Vitamin-E blended highly crosslinked polyethylene liners (52 mm diameter) were paired with electron beam physical vapour deposited (EBPVD) CrN coated and uncoated cast CoCrMo heads and tested in a hip simulator under standard and challenging conditions for over 7 million cycles. Under standard conditions no difference was observed in polyethylene wear rates for the two different counterfaces (9.2 and 9.5 mm^3/mc respectively). The introduction of alumina particles achieved substantial damage on the uncoated heads increasing the polyethylene wear rate to 175 mm^3/mc which remained high even after these particles were removed. The increased wear rate was associated with an increase in small, nanometre sized polyethylene particles. The coated components were resistant to this damage and although a small increase in polyethylene wear was observed with the addition of alumina particles, the wear rate returned to initial rates following their removal under simulated walking and jogging conditions. Larger polyethylene wear particles were generated as a result of this damage resistance. CrN coating has been shown therefore to have the potential to reduce clinical wear and may increase the lifespan of the bearing.

Introduction

Polyethylene is a widely used bearing surface in orthopaedics, although its wear has been reported to limit the lifespan of the joint [1]. Advances in polyethylene have focussed on stabilising the material and thereby reducing its wear, through various processing methods including irradiation in an inert atmosphere to produce a range of crosslink densities in the material whilst reducing the likelihood of oxidation over time [2]. Further reduction of the oxidation process has more recently been achieved by introducing antioxidants, often in the form of vitamin-E, into the material during processing ensuring crosslink densities to provide low wear rates are maintained [3,4].

Conventional forms of polyethylene have been shown to be susceptible to roughening of the head counterface. Retrievals have shown Ra values up to 4.3 μm, attributed to third body wear from either bone or bone cement particles, leading to increases in wear and producing greater quantities of *in vivo* particles sized between 0.1-0.5 μm [5]. In order to reduce this wear mechanism, ceramic heads have often been adopted due to their increased scratch resistance. This has been reported to prevent runaway wear during *in vitro* third body studies [6].

The use of ceramics has historically been of concern due to their low fracture toughness and vulnerability to catastrophic fracture [7]. The safe manufacture of a head with no critical flaws has limited the diameter available to 48 mm [8]. A larger diameter might allow for greater range of motion [9] and reduce the clinical risk of dislocation which is a leading cause for revision in metal-on-polyethylene bearings [10]. Ceramic coatings have therefore been proposed as an alternative to provide the bulk characteristics of the metal with the improved scratch resistance of a ceramic. In previously reported hip simulator studies under standard conditions, the adoption of a coated head has shown little improvement in polyethylene wear rates compared with the uncoated metal [11]. These coatings have not resulted in an improved surface finish compared to the uncoated metal as a result of the coating deposition techniques used such as arc evaporative physical vapour deposition (AEPVD), chemical vapour deposition and sputtering [11] which often need post-deposition polishing. Coatings in metal-on-polyethylene combinations have not been extensively tested under adverse conditions in a hip simulator yet some coatings in metal-on-metal bearings have shown failure under adverse conditions [12].

This study considers whether the use of a chromium nitride, CrN, coating can reduce the wear of vitamin-E blended highly crosslinked polyethylene bearings. The hypothesis of this work is that this coating may increase the scratch resistance of the head, preventing damage under adverse conditions and subsequently protecting the bearing from increases in polyethylene wear. In preventing the generation of surface damage, the coating may also prevent the generation of smaller, bioactive particles under these adverse conditions.

Materials and Methods

Eight 52 mm diameter, larger than commercially available, 0.1 wt% vitamin-E blended polyethylene acetabular liners crosslinked at 120 kGy and mechanically annealed (Corin Ltd, UK), were presoaked in pure deionised water for 55 days. Three liners were paired with hot isostatically pressed and solution annealed uncoated cast CoCrMo (ASTM F75) heads (MoP) and four were paired with heads of similar metallurgy coated with CrN to a thickness of approximately 4-7 μm using electron beam physical vapour deposition (EBPVD) (CrNoP) (Tecvac Ltd, UK). These heads were polished after coating to achieve a surface roughness similar to that of the uncoated heads. One liner remained as an unloaded soak control.

The hip bearings were tested in an orbital hip simulator (MTS Systems, USA) for 5 million cycles following ISO 14242-3:2009 [13] (standard conditions). A further one million cycles of testing was then conducted with 0.15 mg/mL of alumina particles (Buehler, USA) ranging in size from 0.68 – 5.30 μm, showing a bimodal particle distribution with modes 0.78 and 3.10 μm, added to the test fluid (third body conditions). A further one million cycles of testing was conducted with the particles removed, following the ISO standard (damaged conditions). Finally, three tests of 14,400 cycles of simulated jogging were completed at speeds of 1, 1.5 and 1.75 Hz as developed by Bowsher and Shelton (2001) [14] to replicate slow, medium and fast jogging respectively.

Wear was determined gravimetrically for the liners at every third of a million cycles up to one million cycles and every one million cycles thereafter. Three millilitres of fluid taken at 1 million cycles or at the end of each test was used to isolate polyethylene particles as described by Billi et al (2011) [15]. These particles were observed on a scanning electron microscope (Jeol Ltd, Japan) with a minimum of 10 images taken to capture at least 250 particles which were counted and Feret's maximum diameter determined using Image Pro Plus Software (Media Cybernetics, USA).

The surface roughness, Ra and Rz, of the heads were determined before and after testing using an optical surface profilometer (Bruker, USA). Five measurements were taken from each head using a 20 x magnification lens within the wear region. Statistical significance between results was determined by performing a Student's t-test ($p < 0.01$).

Results

Under standard conditions, the wear rate of polyethylene was not statistically significantly different between the coated and uncoated heads producing low wear rates of 9.2 ± 0.1 and 9.5 ± 1.2 mm^3/mc respectively. However, wear in the polyethylene bearings paired with the coated heads with the inclusion of alumina particles was lower, in comparison to the uncoated heads, Figure 1. This test protocol doubled the wear of the coated bearings to 18.3 ± 3.1 mm^3/mc compared with an 18 fold increase of 175.3 ± 145.2 mm^3/mc in the uncoated bearings, with one uncoated bearing wearing at a much higher rate than the other two.

After the third body testing, significant damage was observed in the uncoated metal heads showing 2 μm deep abrasive wear scratches on the surfaces, Figure 2A, increasing the mean Rz values but not the Ra values, Table 1. The CrN coated heads showed little damage, Figure 2B, with no overall change in surface roughness values. Testing following the removal of the third body particles resulted in a high wear rate (469.3 ± 466.1 mm^3/mc) in the uncoated MoP bearings due to the damage developed on the heads while the wear rate of the CrNoP bearings were significantly reduced and returned to levels similar to those observed in the initial phase of testing (12.6 ± 3.6 mm^3/mc). Jogging tests did not significantly increase the wear rates compared to those reported in walking tests following the removal of third body particles in either bearing type; the speed of jogging also did not significantly influence polyethylene wear rates, although the test number was small.

The polyethylene particles produced under standard conditions were small, with the majority of particles sized between 0.1 and 0.2 μm in both bearing types, Figures 3A and B. During adverse testing, however, the polyethylene particles produced from the uncoated metal on polyethylene bearings were noticeably smaller; more than 50% of these were less than 0.1 μm, Table 2. These small particles were produced during the introduction of the alumina particles and maintained a similar distribution of smaller polyethylene particles with the removal of the alumina particles from the test fluid although these took the form of a more elongated shape. Jogging resulted in larger particles, closer in size to those produced under standard conditions yet remained elongated in shape. The CrN coating prevented the generation of these smaller particles as the majority of particles remained between 0.1 and 0.2 μm throughout all phases of testing. The lower wear rate and larger particles produced with the CrN coating suggested that fewer particles overall were produced in the adverse testing compared to the uncoated bearings.

Discussion

Vitamin-E incorporated polyethylene has been optimised to provide long term oxidative stability and in the literature available, the wear rates in hip simulator studies have been low, suggesting that the use of larger diameters (over 40 mm) may be possible [4]. One limitation influencing the wear of metal on polyethylene bearings has been the metal surface's inability to resist scratching, a form of damage which has been widely reported at retrieval [5]. The use of ceramic heads, for increased scratch resistance, is generally limited in manufacture to 48 mm diameter [8] and therefore coated metal heads may be a promising alternative allowing for larger diameter bearings.

This study has highlighted the use of a robust ceramic coating to reduce wear in metal on polyethylene bearing; it was conducted on a hip simulator which may not fully represent the range of activities and challenging conditions found clinically in current patients. The use of alumina particles as third body abrasives, although not clinically relevant, has been established as an extreme adverse test model [16]. Retrievals showing third body wear have reported Ra and Rz values between 0.01-0.45 and 0.07-3.46 μm respectively, with even higher roughnesses in dislocated bearings [17]. The damage observed in the current study was shown by an increase in the mean Rz of the metal heads to 2.73 ± 1.13 μm while the Ra remained low (0.02 ± 0.01 μm). The tests reported in the current study have generated clinically relevant roughness, representative of those damaged through third body processes.

The use of a CrN coating on a CoCrMo head against vitamin-E blended highly crosslinked polyethylene has been shown to produce comparable polyethylene wear rates to the uncoated CoCrMo heads under standard conditions, demonstrating no adverse wear outcomes in the adoption of this coating. The low wear rate in both these 52mm diameter bearings was comparable to that reported for a 36 mm diameter polyethylene crosslinked at 95 kGy (10.4 ± 1.6 mm^3/mc [18]). The wear rate was also noticeably lower compared to the 23 mm^3/mc for a previously reported test [11] on 28 mm polyethylene crosslinked at 40 kGy, paired with a CrN coated head using AEPVD rather than EBPVD. The reported surface roughness, Ra, achieved after AEPVD coating with polishing, was 0.03 ± 0.03 μm [19], comparable to the EBPVD coated heads in the current study. However, parameters such as Rt influence polyethylene wear more than Ra [11]; this parameter is influenced by the formation of microdroplets during the coating process which, in some instances may lead to pit formation during polishing. The EBPVD CrN coating exhibited a lower Rz (mean of Rt) than the uncoated heads suggesting that these surface features were not as prevalent as in other previously reported coatings.

The introduction of alumina particles significantly damaged the uncoated heads, displaying Rz values up to 4.85 μm, similar to retrieved bearings [17]. This damage was manifested as small pits, up to 2 μm deep, with unidirectional scratching. The CrN coated heads did not demonstrate any damage and maintained low surface roughness, comparable to pristine metal heads reported both in this study and elsewhere [11]. In the presence of alumina particles, the CrN coating showed polyethylene wear tenfold lower compared with those paired with uncoated heads. The wear rate of polyethylene paired with the CrN coating using third body particles was lower than both 28 mm and 32 mm diameter polyethylene highly crosslinked at 95 kGy paired with uncoated heads under similar conditions (37 and 48 mm^3/mc respectively [16, 20]). The use of alumina particles abrasives suggests that the coating is likely to withstand most clinical conditions. Damage or delamination of coatings has been of particular concern, there have been reports of a titanium nitride coating against polyethylene delaminating in as little as one year of clinical use [21] and the failure of AEPVD CrN coatings was reported under adverse hip simulator conditions [12]. No such damage was observed in the current study. The removal of the third body particles resulted in the return of low wear rates in the polyethylene paired with CrN coated heads under walking and simulated jogging conditions resulting in a 15 to 35 times decrease in wear in comparison to the uncoated heads.

The CrN coating also reduced the generation of smaller particles under adverse conditions. The immune response generated by these particles leads to loosening of the implant [1] and consequent need for revision with a critical number and size of particles required to elicit a response. In conventional forms of polyethylene, it has been observed that smaller particles are more bioactive [22] and therefore the generation of fewer, larger particles as with the CrN coating may increase the lifespan of the implant. Recent biological findings have additionally suggested that the inclusion of vitamin-E into polyethylene may reduce the inflammatory potential of the wear debris [23], representing a further benefit in the adoption of this bearing combination.

Vitamin-E blended highly crosslinked polyethylene can produce low wear rates under standard simulator conditions regardless of head material but this does not fully represent the clinical condition. More severe testing, assessing routes in which wear may increase, needs to be investigated. Bone cement has previously been added to the test fluid of vitamin-E stabilised polyethylene and has shown negligible effect on wear [3] due to the third body being relatively soft and the concentration (0.15 mg/mL) being too low to influence the wear rate of polyethylene crosslinked at 30 kGy [24]. The use of alumina particles at 0.15 mg/mL has produced significant damage in the uncoated heads in the current study suggesting third body damage may occur in vitamin-E stabilised polyethylenes. The use of a scratch resistant, robust coating as described in this study may further enhance the benefits of this optimised polyethylene withstanding clinical abrasive conditions and maintaining larger, and fewer, wear particles to reduce the risk of osteolysis within the lifetime of the implant.

Acknowledgements

We thank Corin Ltd for the supply of test components and Tecvac Ltd for coating the test components and Jay Meswania from University College London for the use of his optical surface profilometer. This work was funded by an EPSRC UK Studentship supported by Corin and by a TSB funded project (BERTI; Project No. 101005).

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Figures

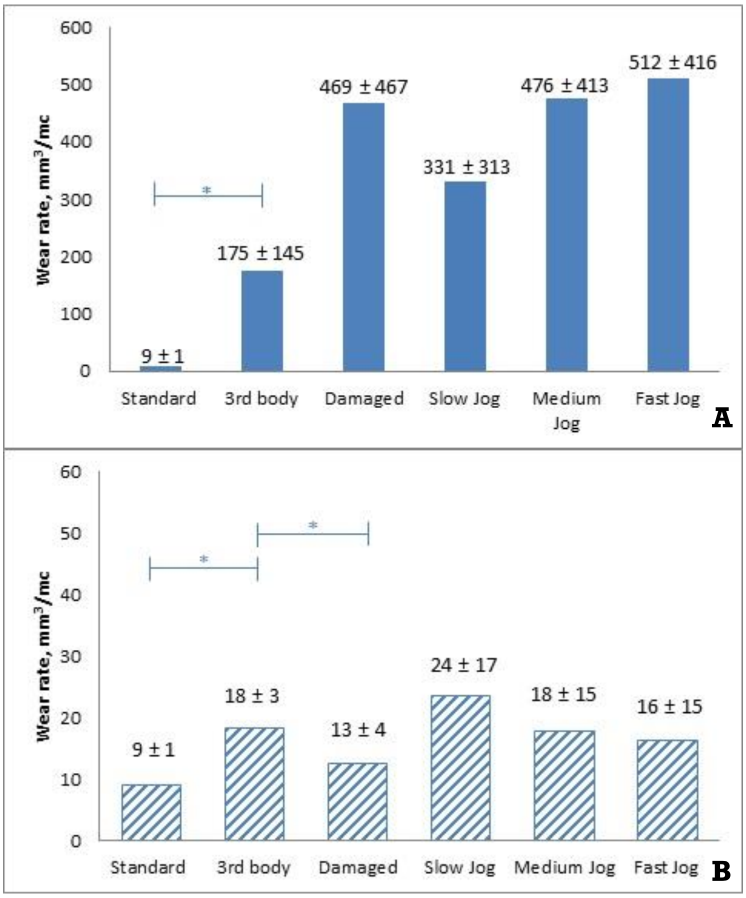

Figure 1. Mean polyethylene wear rates paired with A uncoated cast CoCrMo and B CrN coated cast CoCrMo heads under different test conditions (indicates statistical significance).*

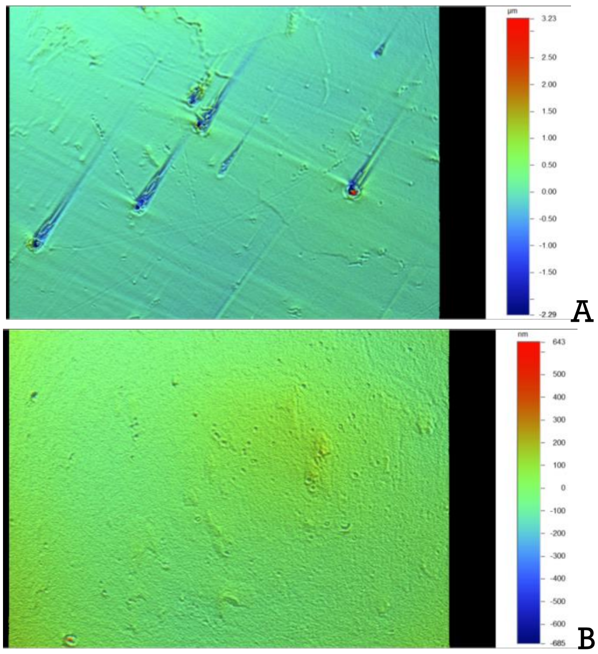

Figure 2A-B. Surface of (A) uncoated cast CoCrMo head and (B) CrN coated cast CoCrMo head following third body testing

Table 1. Changes in surface roughness (mean ± standard deviation) over the full test duration

	MoP		CrNoP	
	Ra, μm	Rz, μm	Ra, μm	Rz, μm
Before testing	0.02 ± 0.01	1.65 ± 0.72	0.01 ± 0.01	0.91 ± 0.52
After third body testing	0.02 ± 0.01	2.73 ± 1.13	0.01 ± 0.003	0.82 ± 0.35
After all testing	0.03 ± 0.01	2.73 ± 1.21	0.01 ± 0.004	0.84 ± 0.64

Table 2. Mode particle size and percentage of particles smaller than 0.1 μm during different test conditions from a minimum of 250 particles

Test	Mode particle size, μm		% of particles < 0.1 μm	
	MoP	CrNoP	MoP	CrNoP
Standard	0.17	0.13	38.7	26.0
3rd body	0.05	0.26	79.0	3.9
Damaged	0.03	0.10	57.6	22.5
Jogging	0.18	0.20	17.2	8.8

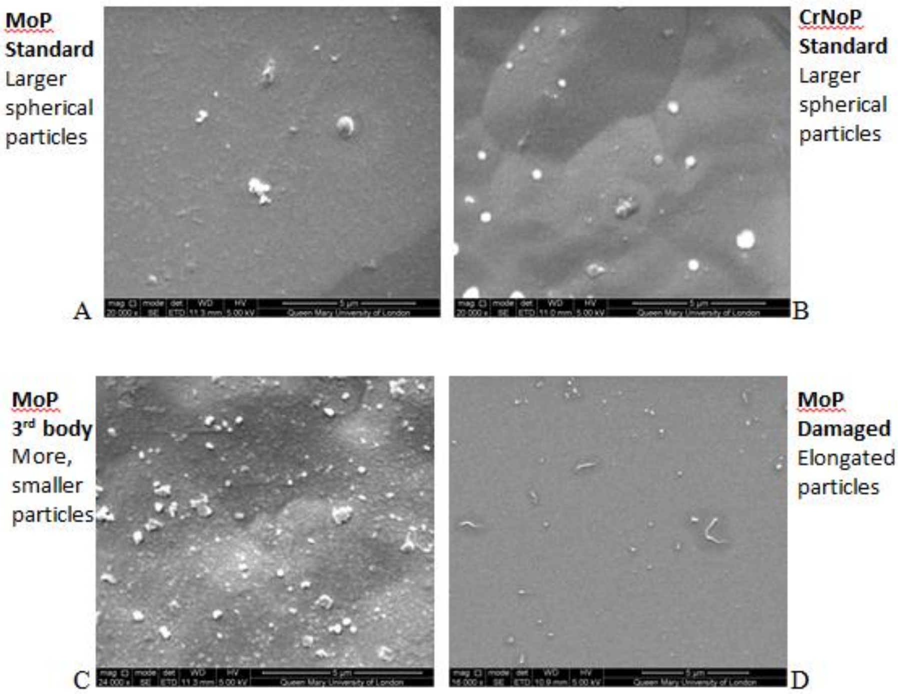

Figure 3. Scanning electron microscopy images taken from (A) cast CoCrMo on polyethylene and (B) CrN coated cast CoCrMo on polyethylene under standard conditions and metal on polyethylene under (C) third body conditions and (D) damage conditionsAFFATATO, S. (ed.) 2012. Wear of Orthopaedic Implants and Artificial Joints, Cambridge: Woodhead Publishing Ltd.

Presentation at Bath Biomechanics Symposium 2013

SEVERE WEAR TESTING OF CHROMIUM NITRIDE COATED AND UNCOATED METAL ON HIGHLY CROSSLINKED VITAMIN-E BLENDED POLYETHYLENE HIP BEARINGS

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Introduction

Developments in polyethylene (PE) quality in recent years, namely irradiation in inert atmospheres to promote crosslinking and the inclusion of vitamin-E to promote long term oxidative stability, have produced low levels of wear in hip simulators under standard conditions [1]. However, historically polyethylene wear has been shown to increase under adverse conditions such as head roughening and jogging [2]. To improve the scratch resistance of the metallic head and therefore reduce wear, the deposition of a ceramic coating on the surface has been proposed [3].
This study considers the influence of adverse testing on metal-on-vitamin-E blended highly crosslinked polyethylene and the use of a chromium nitride (CrN) coating to reduce wear and cobalt (Co) release.

Materials and Methods

Eight prototype 52 mm diameter polyethylene liners were manufactured (GUR 1020 blended with 0.1wt% vitamin-E, crosslinked at 120kGy and mechanically annealed, Corin, UK). Three of the liners were paired with CoCrMo heads (MoP) while 4 were paired with CoCrMo heads coated with CrN by electron beam physical vapour deposition (CrNoP), (Tecvac, UK). One liner remained as an unloaded soak control.
Testing was initially conducted for 5×10^6 cycles (mc) following ISO 14242-3 with a peak load of 3 kN (standard). Non-clinically relevant 3rd body testing using alumina particles added to the test serum (mean size 2.4 μm at a concentration of 0.15 mg/mL) (Bragdon et al., 2004) was then conducted for 1 mc followed by a further 1 mc with the particles removed (worn head). Three jogging intervals of 14,400 cycles were performed with a peak load of 4.5 kN at 1, 1.5 and 1.75 Hz [4]. Wear was measured gravimetrically and fluid samples were used to determine Co release via graphite furnace atomic absorption spectroscopy.

Results

The volume of PE wear for large diameter bearings under standard conditions was not different ($p>0.05$) between head materials (Table 1), however, more ($p<0.01$) head wear and Co release was found for the MoP compared to the CrNoP bearings. Wear increased in both bearings during the 3rd body test compared to standard testing but was much greater in MoP bearings. The increase in metal wear correlated with increased Co release in the MoP bearings; no Co was detected from the CrNoP bearings. Following testing with particles further testing without particles showed the CrNoP to return to steady state wear values in both the liners and heads while the MoP liners continued to wear at a high rate; Co release was greater than standard testing. Jogging did not produce a statistically significant increase in wear rate in either bearing.

Table 1: Mean PE liner and head wear and Co release (± SD) for MoP and CrNoP bearings

Test	PE wear rate, mm^3/mc		Head wear rate, mm^3/mc		Co release rate, ppb/mc	
	MoP	**CrNoP**	**Metal**	**CrN**	**Metal**	**CrN**
Standard (5 mc)	9 ± 1	10 ± 2	0.46 ± 0.04	0.26 ± 0.02	244 ± 63	59 ± 17
3rd body (1 mc)	175 ± 145	18 ± 3	11.32 ± 6.80	0.63 ± 0.07	71900 ± 32300	0
Worn head (1 mc)	469 ± 466	13 ± 4	0.24 ± 0.03	0.13 ± 0.01	850 ± 300	17 ± 5
Jogging (3x 14,400 cycles)	443 ± 381	19 ± 5	-	-	1210 ± 850	83 ± 23

Discussion

Under standard conditions, MoP & CrNoP bearings showed very low wear rates with behaviour similar to 36 mm diameter bearings previously reported [5]. Adverse testing differentiated between the bearings. The improved scratch resistance of the CrN coating, minimised wear during an extreme third body test, which would not occur clinically, but highlighted the robustness of the coating. The reduced wear and Co ion levels throughout testing in these bearings may allow for greater clinical success.

Conclusion

Adverse testing allowed for differentiation between coated and uncoated heads articulating against a wear resistant polyethylene showing the benefits of a CrN coating to reduce wear and Co release.

Acknowledgements

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Presentation at 6th International UHMWPE Meeting 2013

Wear of large diameter vitamin-E blended HXLPE hip bearings against uncoated and chromium nitride coated metal

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Introduction: Polyethylene has been extensively developed since its initial use as a bearing surface in hip replacements in the 1960s, most noticeably in the use of irradiation to produce crosslinks in ultra-high molecular weight polyethylene (UHMWPE). However the degradation of the material over time due to oxidation has been widely reported (Malhotra, 2012) with an early solution to irradiate in inert environments (Peacock and Calhoun, 2006). The introduction of an antioxidant such as vitamin-E has recently been proposed as a method to reduce the formation of free radicals, which are responsible for the oxidation observed, thus providing long term oxidative stability (Oral et al., 2006a).

The occurrence of wear and the resultant wear particles have often been reported to be a limiting factor in the use of metal-on-polyethylene bearings; thus smaller diameter bearings have been used which reduce the sliding distance experienced by a bearing and therefore reduce the wear generated (Charnley et al., 1969). However, the improved wear resistance of highly-crosslinked polyethylene (HXLPE) incorporating vitamin-E may allow for larger diameter bearings to be used, increasing the range of motion possible for a patient, reducing the risk of impingement and dislocation (Burroughs et al., 2005).

Wear reduction of polyethylene liners has also been possible by the adoption of a ceramic head instead of a metallic head (Wang and Essner, 2001). However, the brittle nature of bulk ceramics and the difficulty to manufacture without flaws have up to now limited the use of large head sizes. An alternative is to utilize a ceramic coating on the surface of the metallic head, providing the bulk properties of metal with the improved surface finish and increased abrasion resistance of a ceramic (Galvin et al. 2005b).

Simulator testing of large diameter HXLPE has been reported to produce identical wear rates of 31 mm^3/mc with ceramic and metallic heads under standard conditions therefore requiring adverse testing to distinguish between different head materials (Kubo et al., 2009).

The current study considers the wear of large diameter vitamin-E blended HXLPE bearings paired with uncoated and chromium nitride (CrN) coated metal heads under standard and adverse conditions in a hip simulator. It is proposed that polyethylene wear can be reduced with the adoption of a CrN coated metal head.

Methods and Materials: Eight large (52 mm) diameter non-commercially available polyethylene liners were manufactured for testing purposes (GUR 1020 blended with 0.1 wt% vitamin-E, highly crosslinked at an irradiation dose of 120 kGy and mechanically annealed) (Corin, UK). All liners were presoaked in pure deionized water until their water uptake was stable. Three of the liners were paired with CoCrMo heads (MoP) while four were paired with CoCrMo heads coated with CrN using Electron Beam Physical Vapour Deposition (EBPVD) (CrNoP), (Tecvac, UK). One liner remained as an unloaded soak control.

The bearings were tested in an orbital hip simulator (MTS Systems, USA) for 5 million cycles (mc) under conditions described in ISO 14242-3. Aggressive, non-clinically relevant, third body testing was then conducted for 1 mc to look at the effect of severe head damage. Alumina particles (mean size 2.4 μm at a concentration of 0.15 mg/mL) in the test fluid were used (Bragdon et al., 2003). Subsequently 1 mc of clean testing was conducted before 3 jogging intervals of 14,400 cycles at 1, 1.5, 1.75 Hz (slow, medium and fast respectively) were performed (Bowsher and Shelton, 2001). Wear was measured gravimetrically for both liners and heads throughout testing. Wear debris from fluid samples were analyzed using the protocol described by Billi et al. (2011a).

Results: Wear of the polyethylene liners paired with coated or uncoated heads under standard conditions showed no significant difference with wear rates of 9.2 ± 1.2 and 10.3 ± 1.6 mm^3/mc (mean ± s.d.) respectively (Table 1). Wear of all of the liners increased significantly with the introduction of alumina third body particles and wear of the MoP bearings was approximately ten times higher than CrNoP bearings. The metal heads showed directional grooves caused by the alumina particles while the CrN heads developed no such grooves.

Table 1: Gravimetric wear of highly crosslinked polyethylene liners incorporating vitamin E mm^3/mc (mean ± s.d.)

		MoP	CrNoP
Standard		9.2 ± 1.2	10.3 ± 1.6
3rd body		175.3 ± 145.2	18.3 ± 3.1
Damaged surfaces		469.3 ± 466.1	12.6 ± 3.6
Jogging	**Slow**	330.5 ± 312.6	17.9 ± 16.8
	Medium	475.5 ± 412.2	16.3 ± 14.9
	Fast	512.2 ± 415.8	19.1 ± 15.2

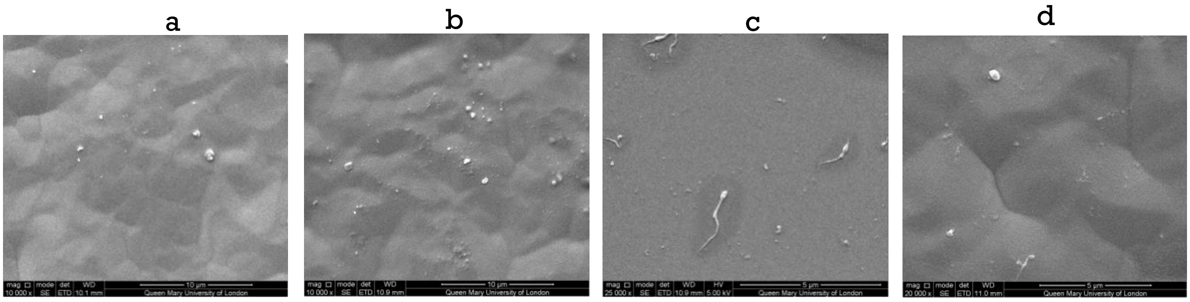

Figure 1: SEM images of particles obtained during a) standard, b) third body and c) damage stages of MoP testing and d) from CrNoP standard testing

After the removal of the 3rd body alumina particles the wear of the CrNoP bearings recovered to wear rates similar to the initial phase of testing. The MoP bearings continued to wear at a higher rate than the CrNoP bearings, due to the damage observed on the heads. Wear of the liners did not significantly increase with the introduction of simulated jogging in either MoP or CrNoP.

Polyethylene particles isolated from all stages of the testing showed a greater percentage of small particles (less than 0.1 μm) present in MoP bearings during severe tests. The shape of these particles were mainly round in standard conditions but during third body and damage tests, elongated and flake particles became more prevalent, Figure 1. The particles from CrNoP bearings showed little difference in size between test conditions with a mode size between 0.1 and 0.2 μm.

Discussion: Wear rates of 52 mm diameter highly-crosslinked vitamin-E blended polyethylene under standard conditions with uncoated or CrN coated CoCrMo heads were comparable to wear rates of 36 mm diameter polyethylene crosslinked at 95 kGy paired with uncoated metal heads (Galvin et al., 2010).

A significant increase in wear rates was observed in both bearing couples during the highly aggressive third body test conditions. The wear rates of the MoP bearings increased 17-fold and were comparable to 28 mm non-crosslinked polyethylene under similar conditions (Bragdon et al., 2003). The introduction of the alumina particles in the test serum represented an extreme, non-clinically relevant test designed to damage the head and severely challenge the bearings. The damage of the head increased wear after the particles were removed but was variable between MoP bearings. The wear rate under these conditions remained higher than tests with moderately or low levels of crosslinked polyethylene against metallic heads similarly damaged (Barbour et al., 2000). Under severe activity, polyethylene liners (Ø28 mm), crosslinked at 50 kGy have previously been shown to produce wear rates as high as 3000 mm^3/mc under fast jogging conditions (Bowsher and Shelton, 2001), therefore the results presented here indicate the potential for highly-crosslinked vitamin-E polyethylene to be used for highly active patients.

The introduction of a CrN coating on the metallic head surface increased the abrasion resistance of the surface preventing runaway wear during adverse tests and maintaining consistently low wear rates. A significant increase in wear rate was established during 3rd body testing compared to standard conditions but a return to the standard rate was observed when the particles were removed. The CrN heads remained smooth with an average surface roughness, Ra, of 0.007 ± 0.003 µm, smoother than many pristine surface coatings (Galvin et al., 2005b, Galvin et al., 2008). The wear rates of the CrNoP bearings were comparable or lower than metal on non-crosslinked polyethylene bearings under standard conditions and lower than 28 mm diameter CrN coated metal on polyethylene crosslinked at 40 kGy (Gavlin et al., 2005b).

Vitamin-E crosslinked polyethylene materials have the potential for use as large diameter bearings although the choice of articulating component needs to be carefully considered. Polyethylene wear is dependent on the head roughness (Bowsher and Shelton, 2001) and thus will increase with surface damage. Retrievals have documented scratching on metallic heads (Tipper et al., 2000) indicating that this is an issue which needs to be addressed. In this study, a robust CrN coating on a CoCrMo substrate has been shown to be resistant to scratching thereby retaining a low polyethylene wear rate. This resistance, even at large diameters, makes a CrN coating promising as a bearing material given problems in fracture and sensitivity reactions reported in large diameter CoC and MoM bearing.

Poster presentation at EORS 2012

Wear of vitamin E blended polyethylene against large diameter CoCrMo metal and EBPVD chromium nitride coated femoral heads

D. de Villiers, A. Fox, L.Morton, S. Collins, J.C. Shelton

Introduction

Metal-on-polyethylene has been the ‘gold-standard‘ in total hip replacement but is limited by wear of the polyethylene cup and the body’s resulting inflammatory response. Crosslinking ultra-high-molecular-weight polyethylene (UHMWPE) reduces wear but concern still remains over oxidation and material degradation. The introduction of an antioxidant (vitamin-E) has been shown to reduce oxidation (Oral et al., 2008).

Attempts to improve the wear resistance of UHMWPE have focussed on improvements to polyethylene, however wear reduction can also be achieved by optimisation of the femoral head component. Coating the femoral heads can decrease the wear of UHMWPE to levels comparable to ceramic-on-polyethylene (Galvin et al., 2005). Equally coating the metal head may reduce Co ion release into the surrounding tissues.

This study investigates the hypothesis that the wear performance of large diameter metal femoral heads articulating against vitamin-E blended UHMWPE can be enhanced by coating with chromium nitride (CrN).

Materials and Methods

Eight 52mm diameter GUR 1020 0.1wt% vitamin-E blended polyethylene liners, crosslinked at a dose of 120kGy and mechanically annealed (Corin, UK) were tested after pre-soaking for 9 weeks. Four were paired with CoCrMo heads and four with electron beam physical vapour deposition (EBPVD) CrN coated heads polished after coating (Tecvac, UK).

Bearings were tested for three million cycles (mc) in an eight station hip simulator (MTS Systems, USA); gravimetric measurements were recorded and cobalt release measured from fluid samples taken over this period using graphite furnace atomic absorption spectroscopy (GFAAS).

Results

The volumetric wear of the vitamin-E polyethylene liners, Figure 1, showed there was no difference between their wear articulating against metal or CrN over 3mc with mean wear rates of 11.11 ± 2.57 and 9.70 ± 1.00 mm^3/mc, respectively.

Both types of femoral head showed measurable wear over the first million cycles with lower wear observed from the CrN heads, Figure 2. The cobalt release (ions and particles) increased over the test period, Figure 3, showing no difference from the CrN heads compared to soak controls.

Discussion

The results from this study show that vitamin-E blended polyethylene is a low wearing polyethylene at large (>50mm) diameters. The use of a coated metallic head compared to the CoCrMo metal had little effect on the wear rate of the liners but did influence the wear of the head itself and may lead to a cycle of increased wear clinically. The initial wear rates of 1.13 ± 0.07 and 0.80 ± 0.03 mm^3/mc for CoCrMo and CrN respectively were similar to standard metal-on-metal (MoM) testing, although mass gain prevented further measurement. Cobalt release from the CrN heads was approximately 20% that from CoCrMo heads and levels were much lower than those reported in MoM (6515 µg/L after 2mc [3]). The lower wear rates and a reduction in metal particle and ion release with CrN coated heads has clinical significance as the release of Co metal ions may be damaging to the surrounding cells.

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Figures:

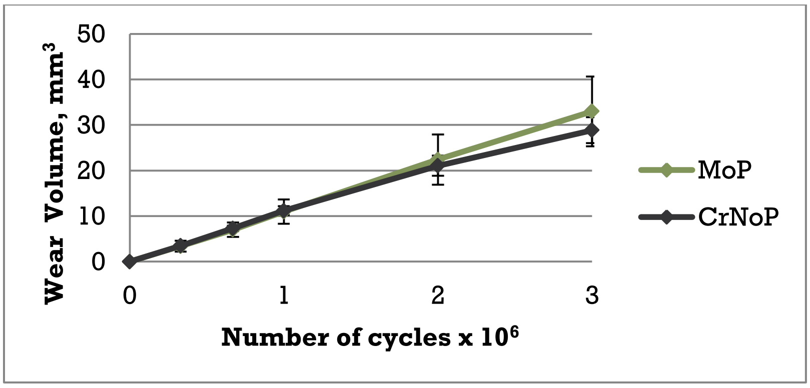

Figure1: Cumulative mean volumetric wear of cups over 3 million cycles (± 1sd)

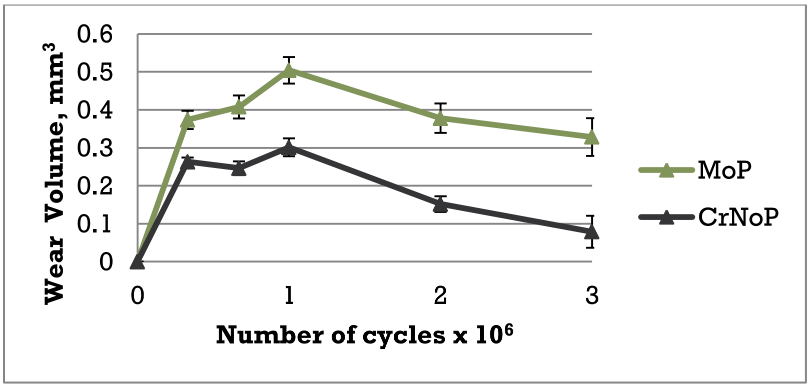

Figure 2: Cumulative mean volumetric wear of heads over 3 million cycles (± 1sd)

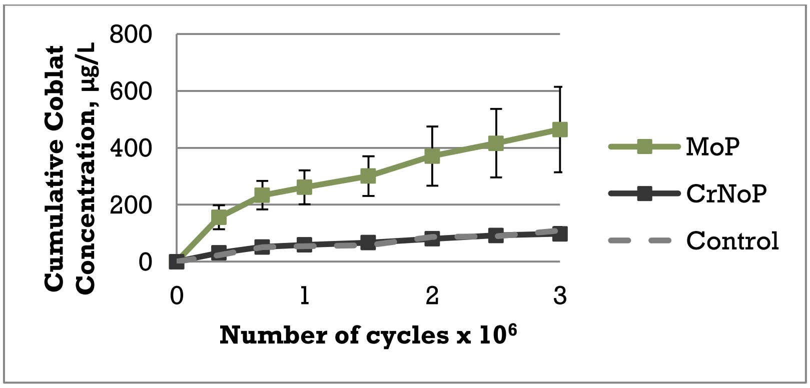

Figure 3: Mean cumulative cobalt release over 3 million cycles (± 1sd)

Poster Presentation ORS 2013

Adverse testing in metal-on-metal and CrN-Ag coated hip replacements

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ABSTRACT BODY:
Introduction: Adverse testing in hip simulator studies has become increasingly important as it has been recognised that standard testing alone does not accurately represent the clinical condition. Growing concern has focused not only on the wear rate but also on the ionic release from metallic bearing surfaces and their wear products. Increased cobalt concentrations have been reported in the blood and urine of patients who have received metal-on-metal (MoM) hip replacements and is currently considered to be the cause of many cases of hypersensitivity, ALVAL and pseudotumours reported [1, 2]. However, tests which have been found to produce more clinically relevant wear rates in MoM bearings such as malpositioning, severe activity and damage have not considered ion release [3, 4, 5]. Coating of these metallic surfaces has been suggested as one method of wear reduction with Electron Beam Physical Vapour Deposition (EBPVD) producing CrN and silver doped CrN coatings capable of reducing wear and cobalt release under standard test conditions [6].

This investigation considers the effect of adverse testing on both the wear and cobalt release of MoM and chromium nitride and silver (CrN-Ag) coated MoM hip replacements.

Methods: 48 mm diameter CoCrMo hip bearings were tested in an orbital hip simulator (MTS Systems, US). Eight pairs were tested as cast (heat treated and solution annealed) MoM (Corin, UK) while five bearings with the same substrate were coated with chromium nitride and 51 wt.% silver via EBPVD (Tecvac, UK). Four test conditions were performed namely standard, lateralisation, high angle, and luxation damage as described in Table 1. Luxation damage was performed after 2.00 mc of high angle testing by displacing the head and cup 27 mm at a force of 2,500 N fifty times [6]. In the lateralisation test, a 0.7 mm lateral displacement of the cup was introduced at swing phase resulting in rim contact at heel strike.

Tests were conducted in newborn calf serum diluted to 25% in pure deionised water with 0.1% sodium azide added to retard bacterial growth. Gravimetric results were taken at 0.17, 0.33, 0.67, 1.00 million cycles (mc) and then every million cycles after that. Fluid samples, taken throughout testing, were used to determine the cobalt concentration via graphite furnace atomic absorption spectroscopy (GFAAS).

Results: Adverse testing conditions increased the wear rate in all MoM bearings, Figure 1. This was greatest in the luxation damage and lateralisation testing. The wear from the CrN-Ag was lower than their MoM equivalents in all cases except one lateralised CrN-Ag bearing which wore at rates comparable to MoM after 1.00 mc, although failure of the coating was not observed.

After 2.00 mc of testing, the total concentration of cobalt released from MoM bearings under adverse conditions was 1.8 to 2.5 times higher than that recorded under standard conditions, Figure 2. The CrN-Ag bearings released substantially less cobalt throughout testing. The lateralised bearing which produced comparable wear rates to metal only released 327.27 μg/L of cobalt over 2.00 mc which correlates to 4% of the cobalt released from standard MoM tests.

Discussion: MoM bearings have the potential to release large amounts of cobalt over their lifetimes. To date, in vitro ion release studies have only focussed on standard hip simulator studies which are already recognised to underestimate the levels of wear in comparison to clinical reports and thus, most likely undervalue the levels of ion release. Adverse conditions in hip simulator studies such as high angle tests and lateralisation have been recognised to increase the wear rate which this study agrees with [3,7]. The increase in wear rate was found to correlate with an increase in cobalt release which suggests that much larger quantities of cobalt may be released than previously thought.

Coating the metallic surfaces successfully decreases both the wear and cobalt release. CrN coatings produced by EBPVD have been shown to reduce wear and cobalt release under standard testing and well as luxation damage conditions in comparison to MoM [6]. The levels of cobalt reported for the CrN-Ag coated components under adverse conditions are approximately 1% of cobalt levels in standard MoM testing. This can provide an effective means of ion release reduction preventing hypersensitivity reactions and damage to the surrounding tissue while withstanding clinically relevant adverse conditions.

Significance: Cobalt ion release is substantially increased in adverse hip simulator testing and the amount released clinically may be higher than originally considered from standard hip simulator tests. It is important that methods to reduce this, such as coating of the metallic surfaces, are investigated and implemented.

Acknowledgements: This work was supported by EPSRC studentships. The authors are grateful to Corin and Tecvac for supplying test components.

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Table 1:Description of parameters used in testing conditions

Test	Bearings tested (n)	Inclination Angle	Swing Phase Load, N	Test duration, mc
Standard	MoM (3)	35°	250	2.00
Lateralisation	MoM (3) CrN-Ag (3)	35°	0	5.00
High Angle	MoM (2) CrN-Ag (2)	60°	250	2.00
Luxation-Repositioning	MoM (2) CrN-Ag (2)	60°	250	2.00

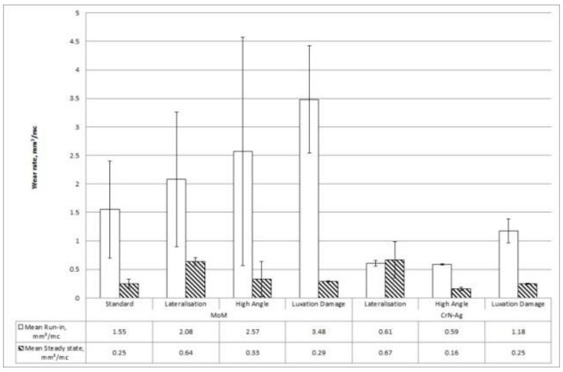

Figure 1: Mean run in (up to 1.00 mc) and steady state (after 1.00 mc) wear rates for MoM and CrN-Ag bearings under different test conditions (± 1 sd)

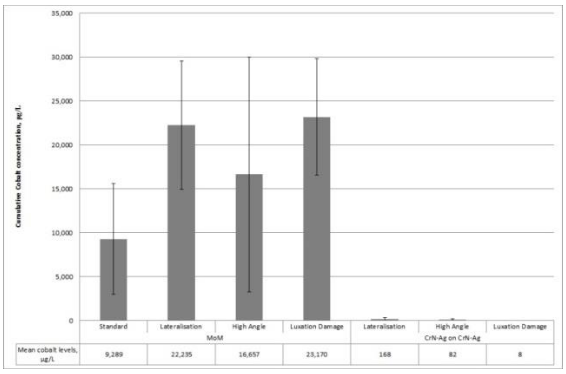

Figure 2: Average cumulative cobalt released after 2.00 mc under different test conditions (±1 sd)

Poster Presentation CORS 2013

Use of Chromium Nitride Coating for the Reduction of Cobalt Release and Metallic Wear in Metal-on-Polyethylene Bearings

D. de Villiers, S. Banfield, J. Housden, A. Kinbrum, A. Traynor, S. Collins, J.C. Shelton

Summary Statement:
Chromium Nitride (CrN) coated and uncoated large diameter metal heads were paired with highly-crosslinked vitamin-E polyethylene and wear tested under a range of adverse conditions. In all conditions, the CrN coating reduced head and cup wear and cobalt release.

Abstract Body:
Introduction
The use of metal-on-metal (MoM) bearings in THRs has highlighted the potential for soft tissue reactions and pseudotumours in the body (Pandit et al., 2008), possibly as a result of corrosion products (cobalt, Co) from the bearing surfaces (Willert et al., 2005). Co release in other bearing combinations has not been widely investigated. Pseudotumours have been reported clinically in metal-on-polyethylene bearings (MoP) and these have recently been attributed to taper corrosion resulting from high torques applied. However, retrievals from MoP bearings have been well documented to show scratching on the metal bearing surface (Bourghli et al., 2010, Tipper et al., 2000). It may be possible to coat metallic surfaces with a ceramic such as CrN, which has been shown in simulator studies to reduce both wear and Co release in MoM bearings, in order to reduce polyethylene wear in MoP bearings (Royle, 2012, Galvin et al., 2005). This investigation examined the influence of head damage on the wear and Co release in MoP bearings under standard and adverse hip simulator conditions for metal and CrN coated counterfaces.

Methods
Seven 52 mm diameter vitamin-E blended highly-crosslinked polyethylene liners, manufactured specifically for testing purposes (not commerically available) (Corin, UK) were tested in a hip simulator. Three of the heads remained as cast, double heat treated metal whilst 4 were coated with CrN (Tecvac, UK). Five million cycles (mc) were completed to ISO 14242-3:2009 followed by 1 mc with alumina 3rd body particles (mean size 2.4 μm, concentration 0.15 mg/mL). These particles are not clinically relevant but were used to look at the effect of severe head damage. A further 1 mc of clean testing was conducted before 3 jogging intervals of 14,400 cycles at 1, 1.5 and 1.75 Hz; slow, medium and fast, respectively.
Wear was measured gravimetrically for the heads. Fluid samples were taken throughout testing for analysis using Graphite Furnace Atomic Absorption Spectrometry (GFAAS) to determine Co release.

Results
Head wear was established for all tests except jogging (Table 1Table). Co release was detected in the fluids from all tests from MoP bearings . Under standard conditions, uncoated heads produced low wear and low levels of Co but adverse testing, initiated by aggresive 3rd body particles, increased head wear and Co release. The CrN coated heads produced less wear and negligle levels of Co throughout.

Discussion/Conclusion

Damage to metallic heads with 3rd body particles, led to Co release in MoP bearings at levels that were higher than have been reported for MoM tests (Royle, 2012); in these tests the Co levels were found to remain relatively high once damage was initiated. The surface roughness following 3rd body damage was similar to those observed from retrievals (Tipper et al., 2000). Coating metal heads with CrN was shown to be an effective method to reduce Co and wear due to its increased scratch resistance. This potentially could reduce the risk of tissue reactions from corrosion products resulting from a single metal bearing surface.

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Tables & Figures:

Table 1: Head wear rates and Co release of uncoated and CrN coated metal heads under standard, third body, damaged and jogging conditions articulating against highly-crosslinked vitamin-E blended polythyelene

Test condition	Metal wear rate, mm^3/mc	CrN wear rate, mm^3/mc	MoP cobalt release rate, ppb/mc	CrNoP cobalt release rate, ppb/mc
Standard	0.46	0.26	244	59
Third Body	11.32	0.63	71892	0
Damaged	0.24	0.13	847	17
Slow Jog			814	225
Medium Jog			867	25
Fast Jog			1956	0

Poster Presentation ISTA 2014

Adverse testing of uncoated and CrN coated metal heads paired with vitamin-E blended highly-crosslinked polyethylene liners

D. de Villiers, A. Kinbrum, A. Traynor, S.Collins, S. Banfield, J.Housden, J.C.Shelton

Introduction

Vitamin-E has been introduced into highly-crosslinked polyethylene liners to reduce the oxidation potential of the material while maintaining low wear rates. However, little has been reported on adverse testing of the material with one test on diffused vitamin-E polyethylene (Oral et al., 2006) and no adverse tests of vitamin-E blended polyethylene reported. Adverse testing of crosslinked polyethylene has focused on the use of large diameters, the incorporation of third body particles, roughening of the counterface or severe activity (Kubo et al., 2009, Bowsher and Shelton, 2001, Barbour et al., 2000). This investigation considers the wear of vitamin-E blended highly-crosslinked polyethylene under standard and adverse conditions articulating against uncoated and chromium nitride (CrN) coated metal heads.

Methods

Seven metal heads were tested against prototype Ø52mm 0.1 wt% vitamin-E blended highly-crosslinked polyethylene liners (Corin, UK). Three heads remained as cast double heat treated metal (MoP) while four, of similar metallurgy, were coated with CrN via electron beam physical vapour deposition (CrNoP) (Tecvac, UK) and polished to a similar surface finish. Tests were conducted for 5 million cycles (mc) under conditions described in ISO 14242-3:2009. Alumina particles (mean size 2.4μm) at concentrations of 0.15 mg/mL were added to the lubricant for 1mc to consider the effect of severe head damage. Testing continued for a further 1mc without the presence of the particles and then 3 jogging intervals (14,400 cycles each) were conducted at slow, medium and fast speeds (Bowsher and Shelton, 2001). Wear volume was determined gravimetrically for the heads and liners and fluid collected throughout the testing was analysed for cobalt concentration using graphite furnace atomic absorption spectroscopy.

Results

Wear rates of the liners were similar under standard conditions for both combinations (Figure 1Table). The introduction of alumina particles created a 17 fold increase in the wear of the MoP liners and increased head wear and cobalt release rates (Figure 2). Damage to the uncoated metal heads was observed as the average surface roughness Ra, of the uncoated heads was rougher (0.018μm) than the coated heads (0.007μm). The CrNoP bearings showed a small increase in liner and head wear but not cobalt release. The removal of the alumina particles saw the CrNoP bearings recover in liner and head wear while wear of the liners and cobalt release remained elevated in MoP bearings. Jogging did not significantly increase the wear of the MoP and CrNoP liners.

Discussion

Under standard testing the use of large diameter MoP appears low wearing, but adverse conditions can increase the polyethylene wear and cobalt release. During the 3^{rd} body testing higher cobalt levels than those reported in adverse metal-on-metal tests (Royle, 2012) were observed, although this test was extreme and not clinically relevant. CrN coating the head showed improved wear resistance and reduced cobalt release during all forms of adverse testing.

Figures:

Table1: Liner wear rates under different test conditions (mean ± sd)

Test condition		MoP wear rate, mm^3/mc	CrNoP wear rate, mm^3/mc
Standard		9.4 ± 0.1	9.2 ± 1.2
3rd body		175.3 ± 145.2	18.3 ± 3.1
Damaged surfaces		469.3 ± 466.1	12.6 ± 3.6
Jogging	Slow	330.5 ± 312.6	17.9 ± 16.8
	Medium	475.5 ± 412.2	16.3 ± 14.9
	Fast	512.2 ± 415.8	19.1 ± 15.2

Table2: Head wear and cobalt release from MoP and CrNoP bearings under different test conditions

Test condition		Metal wear rate, mm^3/mc	CrN wear rate, mm^3/mc	MoP cobalt release rate, ppb/mc	CrNoP cobalt release rate, ppb/mc
Standard		0.46 ± 0.04	0.26 ± 0.02	244 ± 63	59 ± 17
Third Body		11.32 ± 6.80	0.63 ± 0.07	71892 ± 32325	0
Damaged		0.24 ± 0.03	0.13 ± 0.01	847 ± 300	17 ± 5
Jogging	Slow			814 ± 436	225 ± 5
	Medium			867± 585	25 ± 25
	Fast			1956 ± 1544	0

Poster Presentation ORS 2014

The Use of a CrN Coating to Minimise Polyethylene Wear and Cobalt Release in Metal on Vitamin-E Blended Highly Crosslinked Hip Bearings

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Abstract:
Introduction: Developments in the use of polyethylene for total hip replacements have recently focussed on the inclusion of an antioxidant, vitamin-E, to prevent oxidative embrittlement of the material once irradiated [1]. In the limited literature currently available evaluating these materials, bearings have performed well with lower wear rates than conventional polyethylene [2, 3]. This suggests the use of larger diameter bearings may be possible, which would have clinical benefits including increasing the range of motion and reducing dislocation risks. However, full evaluation of this material through a range of tests including adverse testing needs to be considered. Metal-on-conventional polyethylene bearings have been shown to display increased wear rates under 3rd body conditions and simulated jogging, especially when combined with a roughened head counterface [4,5]. Wear reduction has therefore been considered by improving the scratch resistance of the head counterface material by the use of resistant coatings [6]. Coatings have been successfully trialled and reported for metal-on-metal bearings to reduce both metal wear and cobalt ion release [7]. This study considers the wear of large diameter chromium nitride (CrN) coated and uncoated metal on vitamin-E blended highly cross-linked polyethylene under severe 3rd body conditions to evaluate these bearing combinations.

Methods: Eight 52 mm diameter vitamin-E blended polyethylene liners (GUR1020 blended with 0.1wt% vitamin E, irradiated at 120 kGy and mechanically annealed; Corin, UK) were manufactured. These were prototype liners larger than commercially available. The liners were pre-soaked for over 60 days to reach stable fluid absorption. Three liners were paired with as-cast double heat treated CoCrMo heads (MoP) while four liners were paired with heads of a similar metallurgy coated with chromium nitride (CrNoP) by electron beam physical vapour deposition (Tecvac, UK) and polished to reach a similar surface finish to the uncoated heads. One liner remained as an unloaded soak control.

Five million cycles (mc) of testing were completed following ISO 14242-3:2009 in an orbital hip simulator (MTS, US) followed by 1 mc of testing with alumina particles (bimodal distribution with modes of 0.778 and 3.0975 μm, ranging from 0.68 - 5.30 μm) present in the test fluid at a concentration of 0.15 mg/mL. One mc of testing with these particles removed from the test fluid were then conducted followed by three jogging intervals of 14,400 cycles at 1, 1.5 and 1.75 Hz as described by Bowsher and Shelton [5]. Gravimetric wear was measured for both heads and liners and test fluid was taken throughout testing to determine cobalt concentration using graphite furnace atomic absorption spectrometry (GFAAS) (Varian, UK) and to enable wear particles analysis, following a protocol by Billi et al [8], to be performed.

Results: During the initial 5 mc of testing, no statistically significant difference ($p>0.01$) was observed in the mean wear of the polyethylene liners (9 mm3/mc for MoP compared to 10 mm3/mc for CrNoP) however head wear and cobalt release were significantly higher in the uncoated metal (MoP) ($p<0.05$), Table 1. The inclusion of alumina particles into the test fluid greatly increased head and liner wear and cobalt release in the MoP bearings, whilst showing a less marked increase in the CrNoP components. Following removal of particles subsequent tests showed elevated levels of cobalt release and polyethylene wear compared to the initial phase of testing for the MoP components. The polyethylene particles produced during severe 3rd body testing were typically smaller (mean 0.09 μm, mode 0.05 μm) than those produced under standard conditions (mean 0.55 μm, mode 0.17 μm), Figure 1a. Cobalt (Co) release into the fluid linearly correlated with metal wear determined gravimetrically with a Pearson's correlation of 0.99. In

addition higher Co release was correlated with polyethylene wear at the next gravimetric interval throughout all stages of testing (Pearson's correlation of 0.94) allowing polyethylene wear to be predicted based on the previous Co concentration. During the 3rd body testing significant increases in the head and liner wear were observed in the CrNoP bearings however the removal of the particles saw wear rates return to steady state values. Co release remained low, below 100 ppb/mc, even under 3rd body conditions in the CrNoP bearings. Little change in particle size was observed in the CrNoP bearings throughout testing, Figure 1b.
Discussion: Vitamin-E blended polyethylene has been reported to show low wear rates in standard testing promoting its use as a large diameter bearing [2]. In the current work wear rates for 52 mm diameter components (9 mm3/mc) were comparable to 36 mm diameter bearings crosslinked at 95 kGy [9]; however the polymer remains susceptible to roughened conditions creating higher wear. The roughening caused during 1 mc 3rd body testing in this study led to increased polyethylene and Co release even following the removal of these particles in the MoP bearings. The use of alumina particles represents an extreme form of adverse testing, not representative of the clinical condition however results of counterface roughening highlight the value of adverse testing to better understand the wear behaviour of materials. The generation of smaller sized polyethylene particles during this test may suggest increased bioactivity [10] although biological testing on nanometre sized polyethylene particles has not been performed. Despite the extreme conditions created in this study, the CrN coating prevented large increases in polyethylene wear and Co release throughout all stages of testing, with polyethylene wear rates lower than 28 mm diameter coated metal heads against 40 kGy irradiated polyethylene [6]. The CrN coating also prevented the generation of smaller polyethylene particles during adverse testing and therefore may have reduced bioactivity in comparison to those generated in the MoP bearings during the same test conditions. This robust coating may not only allow for the use of large diameter polyethylene bearings, but also minimise the chance of any hypersensitivity reaction caused by the Co release.
Significance: The use of a CrN coating can minimise polyethylene wear and Co release when paired with vitamin-E blended highly crosslinked polyethylene allowing it to be used more safely at large diameters.

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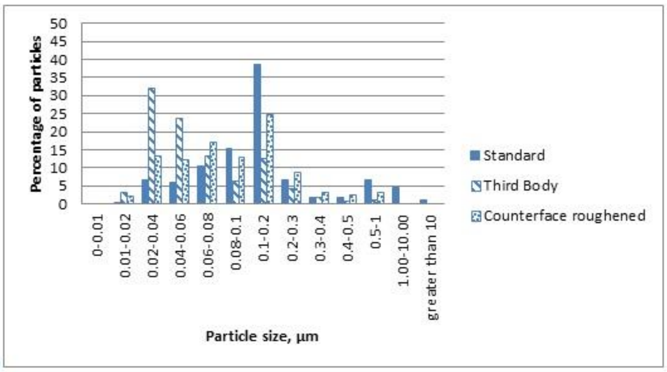
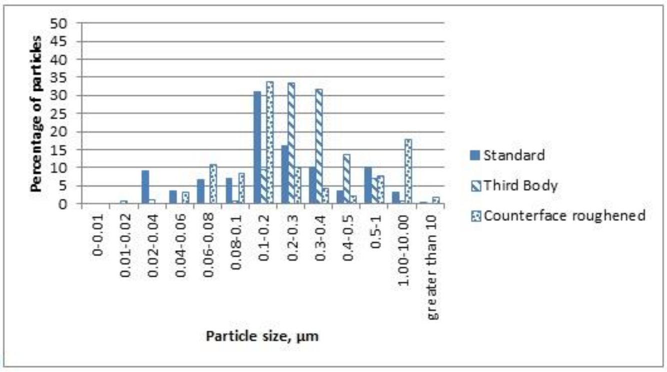
References: 1. Oral et al. (2004) 2. Oral et al (2006) 3. Affatato et al (2010)
4. Bradgon et al (2003)5. Bowsher & Shelton (2001)6. Galvin et al (2005)7. Royle (2012) 8. Billi et al (2011) 9. Galvin et al (2010) 10. Green et al (1998)



a)



b)

Figure 1: Particle distribution of polyethylene particles produced under different test conditions from a) metal- b) CrN coated metal-on-vitamin E blended highly cross-linked polyethylene, for 3 loading conditions

Table 1: Mean PE liner and head wear and Co release (± SD) for MoP and CrNoP bearings

Test	PE liner wear rate, mm^3/mc		Head wear rate, mm^3/mc		Co release rate, ppb/mc	
	MoP	CrNoP	Metal	CrN	Metal	CrN
Standard (5 mc)	9 ± 1	10 ± 2	0.46 ± 0.04	0.26 ± 0.02	244 ± 63	59 ± 17
3rd body (1 mc)	175 ± 145	18 ± 3	11.32 ± 6.80	0.63 ± 0.07	71900 ± 32300	0
Counterface roughened (1 mc)	469 ± 466	13 ± 4	0.24 ± 0.03	0.13 ± 0.01	850 ± 300	17 ± 5
Jogging (3x 14,400 cycles)	443 ± 381	19 ± 5	-	-	1210 ± 850	83 ± 23

Poster Presentation EFORT 2014

Wear Reduction in Polyethylene through the adoption of scratch resistant CrN coatings

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Introduction

The latest generation of highly crosslinked polyethylene to include vitamin-E has optimised the oxidative stability of the material while maintaining mechanical properties and wear reduction (Oral et al., 2006). However, it is well established that polyethylene wear is often substantially increased when the counterface surface is roughened (Barbour et al., 2000). Therefore, the improvements in long term clinical performance predicted through the use of vitamin-E blended polyethylene in hip simulator studies may not fully represent the clinical situation when roughening of the head may occur. Increasing the scratch resistance of the head surface by coating it with a ceramic may reduce wear through improved surface finish and reduce cobalt release (Royle, 2012) as well as improving the bearing's resistance to surface damage.

Objectives

To determine whether under aggressive, abrasive hip simulator conditions polyethylene wear can be reduced through the adoption of a chromium nitride coating.

Methods

Seven 52 mm diameter 0.1 wt% vitamin-E blended highly crosslinked polyethylene liners (Corin Ltd, UK) were tested in a hip simulator. Three liners were paired with uncoated CoCrMo heads while the remaining four were paired with CoCrMo heads coated with CrN using electron beam physical vapour deposition (Tecvac Ltd, UK) and polished after coating. These were tested for 5 million cycles (mc) under ISO 14242-3 (2009) conditions; subsequently 1 mc of testing using alumina particles added to the test fluid (concentration of 0.15 mg/mL) were conducted followed by a further 1 mc of testing with the particles removed. Wear of the liners was determined gravimetrically and fluid taken throughout testing was analysed for cobalt.

Results

Under standard conditions, the polyethylene wear was low (10 mm^3/mc) whether paired with uncoated or CrN coated metal heads. There was no significant difference in the polyethylene wear rates but cobalt released over 5 mc was reduced with the use of the coating (660 ppb to 130 ppb). The inclusion of the alumina particles increased the polyethylene wear rate (175 mm^3/mc) when paired with uncoated heads due to scratching of the metallic heads and associated high levels (70,700 ppb) of cobalt release. The CrN coating was resistant to this damage with only a small increase in the polyethylene wear rate (18 mm^3/mc) and no cobalt release. The removal of alumina particles saw the polyethylene wear rate return to that observed initially in liners paired with the CrN coated heads and in these bearings less cobalt was released (16 ppb). The damage on the metallic heads resulted in significant increase in wear (469 mm^3/mc) after the third body particles were removed and cobalt was released at an increased rate (838 ppb/mc compared to 131 ppb/mc in initial standard conditions).

Conclusions

Vitamin-E highly crosslinked polyethylene wear is susceptible to roughening as has been observed in previous forms of polyethylene (Bowsher & Shelton, 2001). Whilst the current generation of polyethylene may have a lower biological activity (Bladen et al., 2013) compared to traditional polyethylene, the limitations in the success of this material will be related to counterface damage. Combining polyethylene with a metal head can increase polyethylene wear and release cobalt once damage is initiated. Therefore, the adoption of a scratch resistant head material, such as a CrN coating which exhibits excellent adhesion to the metallic surface, may be necessary to further improve the use of polyethylene in orthopaedic bearings.

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Determining appropriate adverse testing for coated metal-on-polyethylene hip bearings

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The need for appropriate laboratory adverse wear tests of hip replacements has been highlighted. Retrieved metal-on-polyethylene (MoP) components have shown extensive scratching on the heads which increases polyethylene wear contributing to the need for revision. Coating the metal surface for increased scratch resistance has been proposed although, delamination of the coating leading to excessive wear (Leslie et al., 2013) remains a concern. The introduction of 3rd body particles to hip simulator test fluid has been shown to increase wear rates for standard MoP components, whilst edge loading for these components is not damaging.

Large diameter uncoated Co-Cr-Mo metal-on-vitamin-E blended highly crosslinked polyethylene (Corin Ltd, UK) bearings were tested in a hip simulator under standard conditions (Figure 1) with the majority of polyethylene particles isolated from the fluid sized 0.1-0.2μm. Testing with bone cement particles (concentration: 5mg/mL) doubled the wear rate but did not alter the particle distribution; adding alumina particles (concentration: 0.15mg/mL) increased the wear rate 15x, producing more particles <0.1μm and generated extensive head roughening (Rz 2.73μm). The difference in the resultant head damage led to differences in wear rates following removal of these particles. Alumina damaged bearings wore highly, producing small particles, whilst those tested with the bone cement returned to standard wear behaviour.

Chromium nitride coating applied by EBPVD (Tecvac Ltd, UK) of large diameter bearings (CrNoP) showed no difference in wear performance compared to MoP bearings under standard conditions. Alumina particles added to the test fluid doubled the wear rate but wear particles generated remained >0.1μm. Inspection of the CrN coated heads showed no damage (Rz 0.82μm); a low wear rate was recorded when the particles were removed.

Whilst both bone cement and alumina particles increased wear rates in MoP bearings, alumina was a much more severe test, damaging both the polyethylene and the head and resulting in increases in polyethylene wear even once the particles were removed. Whilst the alumina particles test is not clinically relevant, the ability of the coating to withstand this damage, indicates improved scratch resistance and the robust nature of the coating, potentially capable of withstanding adverse, unpredicted clinical conditions.

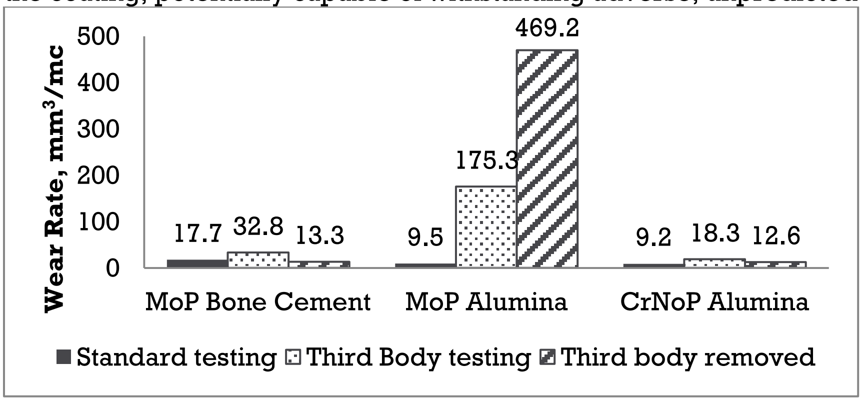

Figure 1: Mean wear rates of uncoated and coated metal-on-polyethylene bearings under standard, third body and particles removed conditions

Reference: LESLIE, I., WILLIAMS, S., ISAAC, G., HATTO, P., INGHAM, E. & FISHER, J. 2013. Wear of surface-engineered metal-on-metal bearings for hip prostheses under adverse conditions with the head loading on the rim of the cup. *Proceedings of the Institution of Mechanical Engineers 227(4) 345-9.*